About the Book

In the first part of this book, classical nonequilibrium statistical mechanics is developed. Starting from the Hamiltonian dynamics of the molecules, it leads through the irreversible kinetic equations to the level of fluid mechanics. For simple systems, all the transport coefficients are determined by the molecular properties.
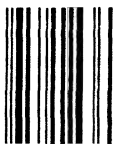
The second part of the book treats complex systems that require a more extensive use of statistical concepts. Such problems, which are at the forefront of research, include: continuous time random walks, non-Markovian diffusion processes, percolation and related critical phenomena, transport on fractal structures, transport and deterministic chaos. These "strange transport processes" differ significantly from the usual (diffusive) transport. Their inclusion in a general treatise on statistical mechanics is a special feature of this invaluable book.

About the Author

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STATISTICAL DYNI

Matter out of Equil

Radu Balescu

STATISTICAL DYNAMICS
Matter out of Equilibrium

Contents

Chapter 1

Introduction

When I was invited to consider writing a new book on non-equilibrium statistical mechanics, it did not take me much time to reach a positive decision. Several factors encouraged me to accept this challenge.

1) During my whole scientific life I have been deeply fascinated by the various aspects of our understanding of the macroscopic phenomena in terms of the behaviour of the underlying atoms or molecules. The *equilibrium properties* of matter (i.e., of a collection of N "atoms" enclosed in a region of volume V, where $N \gg 1$ and the volume is much larger than the volume of an atom) were already clearly formulated by *Gibbs* (1902) at the beginning of this century. The remarkable beauty of equilibrium statistical mechanics lies in the fact that *a single formula allows the calculation of all thermodynamical quantities from the input of the Hamiltonian, which defines in a nutshell the dynamics of the molecules.* If we ask, however, *how* the thermal equilibrium is reached (*if* it is reached at all) from an arbitrary starting point, this extraordinary simplicity no longer exists. A much more detailed study of the dynamics is now necessary, and this leads to an enormously more complex situation. It is precisely this feature which makes non-equilibrium statistical mechanics still a challenging field.

2) In 1963 I wrote a book on *Statistical Mechanics of Charged Particles* in which an early version of the new formalism (at that time) developed in Brussels for the non-equilibrium theory found a non-trivial application to plasmas. The latter systems offer an enormous amount of problems of highest interest, both for their theoretical and their practical importance.

3) In 1975 I published a rather voluminous treaty of *Equilibrium and Non-equilibrium Statistical Mechanics.* In this book, the main problems of the field were extensively treated. The non-equilibrium part of the book (almost one half) was developed in great detail, with an exposition of the derivation and the use of the "classical" kinetic equations for dilute gases, weakly coupled systems and plasmas. The matter was presented up to the end stage, i.e., the calculation of transport coefficients. This is the

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Chapter 2

States, Dynamical Functions, Evolution

2.1 General Considerations

The main object of study in the present book is the evolution in time of a *dynamical system*. In the present context this concept will be defined as *a certain amount of matter*. Note that the concept of a dynamical system can be used in a wider meaning: it could apply to non-material systems, such as radiation. In the modern literature on nonlinear physics, it is given a much more abstract meaning: in this context, a dynamical system is merely a set of equations defining a law of evolution of some mathematical functions of "time". Statistical dynamics can be generalized in order to cover such systems as well. Problems of this type will be discussed in Chap. 15. At present, however, we limit ourselves to the study of material systems.

Matter can be studied at two different levels. At the *macroscopic level* the system is described in the form that is directly accessible to our senses. Typical examples are: a certain amount of gas or of liquid enclosed in a vessel (which defines its volume), or a piece of solid material. At the *microscopic level* the same system is described as a collection of an extremely large number of atoms or of molecules interacting with each other through well-defined mechanical forces.[1]

Before starting the detailed study of any dynamical system, three concepts must be defined: the *state*, the *dynamical functions* and the *law of evolution*.

The STATE of a system is determined by *the specification of a fixed set of basic*

---

[1] Note that the key concept here is the large number of particles, not their small size. The difference between "macroscopic" and "microscopic" levels is essentially relative. As an example, a star is a macroscopic mass of gas composed of a very large number of molecules interacting through intermolecular forces of quantum electrodynamical nature. But the same star can also be considered globally as a point particle interacting through gravitational forces with many other stars within a galaxy.

physical quantities. The number and the nature of these quantities must be such as to determine uniquely all the present properties of the system and as to allow a unique prediction of its future evolution. Technically speaking: if a set of values of these quantities is taken as initial values adjoined to the equations of evolution of the system, a well-posed mathematical problem is obtained.

Any physical quantity, different from those defined above, takes (in general) a uniquely determined value as soon as the state of the system is defined (i.e., when the basic quantities have a specified value). These quantities are thus described as *functions (or functionals) of the basic state variables*. They will be called DYNAMICAL FUNCTIONS.

Finally, the LAW OF EVOLUTION is required for completing the description of the system. It determines the transformation in time of the state of the system, hence of its dynamical functions. It can be expressed by a differential equation, or a partial differential equation, or a finite-difference equation, or an integral equation: we will meet with examples of all these kinds.

The nature of the states, of the dynamical functions and of the law of evolution is widely different according to the level of description. The object of statistical dynamics is to provide a link between the microscopic and the macroscopic levels. In the present chapter, we recall briefly the description of a dynamical system at these two levels. These may be considered, respectively, as the input and the output of statistical mechanics.

2.2   Macroscopic Dynamical Systems

In order to fix the ideas, the dynamical system considered in the first place is *a one-component fluid*. In the macroscopic context, the fluid is viewed as a continuous medium. The physical quantities associated with the system must therefore be specified in every point of the physical space. They are therefore *fields*, i.e., functions of the physical space coordinates x and of the time t.

The hydrodynamical *state* is defined by the specification of two scalar fields: the mass density $\rho(x,t)$ and the temperature $T(x, t)$, and a vector field: the local velocity $u(x, t)$:

$$\rho(x, t), \quad u(x, t), \quad T(x, t) . \tag{2.1}$$

If the hydrodynamical description is valid (the answer to this question will be provided by statistical dynamics, see Chap. 10), all other physical quantities must be regarded as *dynamical functions* of these three basic state variables.

The *law of evolution* is provided by the equations of hydrodynamics which describe the evolution in time of the hydrodynamical state variables. These equations are

simply expressions of the conservation of mass, momentum and energy: we assume that the reader is familiar with these equations (see references at the end of this chapter); they will be derived from a microscopic theory in Chap. 10. The equations of evolution are balance equations for the mass density ρ, the momentum density $\rho\mathbf{u}$ and the internal energy density ρe (i.e. the density of the total energy minus the kinetic energy, minus the potential energy)[2]:

$$\partial_t \rho = -\nabla \cdot (\rho\mathbf{u}) \,, \tag{2.2}$$

$$\partial_t \rho\mathbf{u} = -\nabla \cdot [\rho\mathbf{uu} + P\mathbf{l} + \pi] \,, \tag{2.3}$$

$$\partial_t \rho e = -\nabla \cdot [\rho e\mathbf{u} + \mathbf{q}] - P\nabla \cdot \mathbf{u} - \pi : \nabla\mathbf{u} \,. \tag{2.4}$$

Here $P(\mathbf{x}, t)$ is the scalar pressure, $\mathbf{l}$ is the unit tensor, $\pi(\mathbf{x}, t)$ is the dissipative pressure tensor and $\mathbf{q}(\mathbf{x}, t)$ is the heat flux.

Eqs. (2.2) - (2.4) exhibit the well-known difficulty of macroscopic hydrodynamics: these equations are not closed. In order to obtain well-defined equations, the pressure P, the internal energy (per unit mass) e, as well as the dissipative pressure tensor π and the heat flux $\mathbf{q}$ must be defined as dynamical functions, i.e., as functions of the state variables ρ, $\mathbf{u}$, T. In the framework of macroscopic physics, this closure operation can only be performed empirically, on the basis of experimental evidence and of some symmetry considerations. One of the main purposes of statistical dynamics will be the justification and the definition of the domain of validity of such hypotheses. Specifically, there are two types of phenomenological assumptions used in the closure of the hydrodynamical equations.

Equations of State

It is assumed that the *pressure* and the *internal energy density* depend on $\mathbf{x}$ and t only through the mass density $\rho(\mathbf{x}, t)$ and the temperature $T(\mathbf{x}, t)$, i.e. two of the hydrodynamical variables[3]:

$$\begin{aligned}
P(\mathbf{x}, t) &= P[\rho(\mathbf{x}, t), T(\mathbf{x}, t)] \\
e(\mathbf{x}, t) &= e[\rho(\mathbf{x}, t), T(\mathbf{x}, t)]
\end{aligned} \tag{2.5}$$

It is, moreover, assumed that the functions $P(\rho, T)$ and $e(\rho, T)$ have the same form as in thermal equilibrium. For instance, for a dilute gas, one would assume

---

[2]Whenever no ambiguity is possible, we omit writing the variables $(\mathbf{x}, t)$ explicitly.

[3]These quantities are independent of the velocity $\mathbf{u}$, because the kinetic energy density $\frac{1}{2}\rho u^2$ has been subtracted from the total energy (see also Sec. 10.1).

$P(\mathbf{x}, t) = \rho(\mathbf{x}, t)\, RT(\mathbf{x}, t)$, where R is the well known gas constant. Note also that the second relation (2.5) allows us to transform the internal energy balance equation (2.4) into an equation for the temperature. This *local equilibrium hypothesis* can be interpreted as follows: in a small region around each point, a state close to equilibrium is reached, but the parameters (density and temperature) of this pseudo-equilibrium state vary slowly (compared to molecular space- and time-scales) from one point to another (see Sec. 9.5).

Transport Equations

The dissipative pressure tensor π and the heat flux $\mathbf{q}$ are related, respectively, to the velocity gradient and to the temperature gradient. More precisely, if $\{\nabla\mathbf{u}\}^{o} = \nabla\mathbf{u} + (\nabla\mathbf{u})^{T} - \frac{2}{3}(\nabla\cdot\mathbf{u})\,\mathsf{I}$ is the symmetric traceless part of the velocity gradient tensor[4], the following relations are often assumed:

$$
\begin{aligned}
\pi &= -\eta\,\{\nabla\mathbf{u}\}^{o} - \zeta\,(\nabla\cdot\mathbf{u})\,\mathsf{I} \\
\mathbf{q} &= -\kappa\,\nabla T
\end{aligned}
\tag{2.6}
$$

These TRANSPORT EQUATIONS [5]establish a *linear* relationship between the nonequilibrium response of the system, measured by the *fluxes* $\pi, \mathbf{q}$ of momentum and of heat, and the *thermodynamic forces* characterizing the spatial inhomogeneity of the system. The coefficients entering these equations (assumed to be constant in space and time) are called the *transport coefficients*: they are given specific names. η is the *shear viscosity* (or simply, viscosity) coefficient, ζ is the *bulk viscosity* coefficient, and κ is the *thermal conductivity* coefficient. All these coefficients must have a definite positive sign, required by the Second Law of Thermodynamics. Eqs. (2.6) are also called, respectively, the Navier-Stokes and the Fourier transport equations.

Substituting Eqs. (2.5), (2.6) into the balance equations (2.2)-(2.4) we obtain [introducing the specific heat at constant volume $c_V = (\partial e/\partial T)_\rho$]:

$$
\partial_t \rho = -\nabla\cdot(\rho\mathbf{u}) \quad,
\tag{2.7}
$$

$$
\begin{aligned}
\partial_t \mathbf{u} &= -(\mathbf{u}\cdot\nabla\mathbf{u}) - \frac{1}{\rho}\left(\frac{\partial P}{\partial\rho}\right)_T \nabla\rho - \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho \nabla T \\
&\quad + \frac{\eta}{\rho}\nabla^2\mathbf{u} + \frac{\zeta + (1/3)\eta}{\rho}\nabla(\nabla\cdot\mathbf{u}) \quad,
\end{aligned}
\tag{2.8}
$$

---

[4]$(\nabla\mathbf{u})^{T}$ denotes the transposed velocity gradient tensor; thus: $(\nabla\mathbf{u})_{ij} = \nabla_i \mathbf{u}_j$, $(\nabla\mathbf{u})^{T}_{ij} = \nabla_j \mathbf{u}_i$.

[5]They are also called "phenomenological equations" in books of nonequilibrium thermodynamics. The name is not quite appropriate in the context of statistical mechanics, where these relations are derived from first principles.

$$\partial_t T = -(\mathbf{u} \cdot \nabla)T - \frac{T}{\rho c_V}\left(\frac{\partial P}{\partial T}\right)_\rho (\nabla \cdot \mathbf{u}) + \frac{\eta}{\rho c_V}\{\nabla \mathbf{u}\}^o : \{\nabla \mathbf{u}\}^o$$

$$+ \frac{1}{\rho c_V}\left(\zeta - \frac{2}{3}\eta\right)(\nabla \cdot \mathbf{u})^2 + \frac{\kappa}{\rho c_V}\nabla^2 T \qquad (2.9)$$

This is the final, closed set of *hydrodynamical equations* for a simple neutral one-component fluid. Clearly, for different types of systems (e.g., multicomponent fluids, plasmas, non-newtonian fluids), the equations of state and the transport equations have to be modified and the final equations (2.7) - (2.9) will take a more complicated form.

We now discuss a fundamental property of these macroscopic equations. Consider the following mathematical transformation, called the *time inversion:*

$$T : \begin{pmatrix} t \Rightarrow -t \\ \mathbf{u} \Rightarrow -\mathbf{u} \end{pmatrix} \qquad (2.10)$$

Under this transformation, Eq. (2.7) is invariant, but Eqs. (2.8), [2.9] are not: the terms containing a transport coefficient are odd [even], whereas the remaining terms are even [odd]. *The hydrodynamic equations are NOT invariant under the time inversion transformation. They describe an* IRREVERSIBLE *evolution process.* The reversibility is broken by the presence of the terms containing transport coefficients: these are also called *dissipative terms*. The existence of irreversibility poses the most serious problem of principle to nonequilibrium statistical physics. The main program of the latter science is the derivation of the macroscopic laws of evolution from the microscopic ones. But the latter, as will be seen below, are reversible! It will be seen in the forthcoming chapters how one can give a beginning of an answer to this difficult paradox, at least in some important special cases.

2.3 Microscopic Dynamical Systems

At the molecular level the dynamical system considered in the previous section is described as an assembly of $N \gg 1$ discrete molecules, rather than a continuous distribution of matter. We assume again that we deal with a one-component system, hence all its molecules are identical. For simplicity, we also assume that the molecules are idealized as point particles. The generalization to the case of several species or to the consideration of internal degrees of freedom of polyatomic molecules is not difficult, in principle, but will not be discussed here (see Secs. 5.3, 5.4).

As explained in the introduction, we deliberately assume that the motion of the molecules is governed by the laws of classical mechanics. Although this is not fundamentally correct, it turns out that for many problems of nonequilibrium statistical

mechanics it is a sufficient approximation. In particular, the explanation of the "irreversibility paradox" does not specifically require a quantum mechanical description.

We use here the *Hamiltonian version of classical mechanics*, which is particularly well adapted to the problems of statistical physics. (More details can be found in the references quoted at the end of this chapter). Each particle, labelled j ($j = 1, 2, ..., N$), is characterized by the coordinates of its position $\mathbf{q}_j$ and by its conjugate momentum $\mathbf{p}_j$: these are three-vectors, i.e., a point particle has three degrees of freedom. The complete specification of the *state* of the dynamical system requires the knowledge of all the coordinates and of all the momenta: $(\mathbf{q}_1, ..., \mathbf{q}_N, \mathbf{p}_1, ..., \mathbf{p}_N)$, i.e. of $2F = 6N$ data (F is the number of degrees of freedom). A natural representation of this situation is obtained by defining an abstract *phase space* spanned by the F coordinates and the F momenta. The instantaneous state of the system is described by a point in the $2F$–dimensional phase space. In forthcoming formulae we will most often use either one of the following useful abbreviations:

$$(q_1, ..., q_F, p_1, ..., p_F) = (\mathbf{q}_1, ..., \mathbf{q}_N, \mathbf{p}_1, ..., \mathbf{p}_N) \equiv (q, p) \equiv (x_1, ..., x_N) \qquad (2.11)$$

where q [p] represents the set of $3N$ coordinates [$3N$ momentum components] of all the particles, whereas x_j represents the set of 3 coordinates and 3 momentum components of particle j .

The *dynamical functions* appear naturally as the set of functions on the phase space: $B(q, p)$. An important special case is the total energy of the system, consisting of kinetic energy and of potential energy of interaction (in absence of an external field). The total energy is further assumed here to be time-independent (conservative system)[6]: it represents the HAMILTONIAN of the system, $H(q, p)$. Its specific form will be discussed in Sec. 2.4.

During the motion, the positions of the particles and their momenta change and become functions of time: $q(t)$, $p(t)$. The *law of evolution* determining these functions of time is the set of *Hamilton's equations of motion* of classical mechanics:

$$\frac{dq_j(t)}{dt} = \frac{\partial H(q, p)}{\partial p_j} \ , \quad \frac{dp_j(t)}{dt} = -\frac{\partial H(q, p)}{\partial q_j} \ . \qquad (2.12)$$

One should carefully avoid a common misunderstanding: $q(t)$, $p(t)$ are not to be confused with q, p. The latter are invariable coordinates of the phase space, representing the positions and momenta at a given time, e.g., $t = 0$. On the contrary, $q(t)$, $p(t)$ are dynamical functions, obtained by solving the equations of motion with q, p as initial conditions, thus: $q(t) = q(q, p; t)$, $p(t) = p(q, p; t)$. The ordered set of points $q(t)$, $p(t)$ for $-\infty < t < \infty$ defines the *orbit* of a system in phase space.

---

[6]In some problems, to be treated in subsequent chapters, we will also consider the action of a time-dependent external field, in which case the present formalism has to be slightly generalized.

Consider now an arbitrary dynamical function $b(q,p)$ that does not depend explicitly on time. Its value will change during the motion because the coordinates and the momenta are changing. We therefore introduce a function $b(q,p;t) \equiv b(q(t), p(t))$; its time dependence is determined by the following equation:

$$
\begin{aligned}
\partial_t b(q,p;t) &= \sum_{j=1}^{F} \left\{ \frac{\partial b}{\partial q_j} \frac{dq_j}{dt} + \frac{\partial b}{\partial p_j} \frac{dp_j}{dt} \right\} \\
&= \sum_{j=1}^{F} \left\{ \frac{\partial b}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial b}{\partial p_j} \frac{\partial H}{\partial q_j} \right\} \quad (2.13)
\end{aligned}
$$

In the last expression one immediately recognizes the familiar form of the *Poisson bracket* of the dynamical functions b and H (in this order):

$$
\partial_t b(q,p;t) = [b, H]_P. \quad (2.14)
$$

The Poisson bracket is an operation involving a couple of dynamical functions; it has the following algebraic properties [here $a, b, c, \ldots$ are dynamical functions and $\alpha, \beta, \ldots$ are scalars, i.e. quantities that are independent of q, p]:

$$
[a, b]_P = - [b, a]_P
$$

$$
[\alpha, b]_P = 0
$$

$$
[ab, c]_P = a [b, c]_P + [a, c]_P \, b
$$

$$
[a, [b, c]_P]_P + [b, [c, a]_P]_P + [c, [a, b]_P]_P = 0. \quad (2.15)
$$

Because of these properties, the Poisson bracket appears as a particular realization of an abstract *Lie bracket*. We now postulate that the set $\mathcal{D}$ of all dynamical quantities is endowed with this Lie bracket operation, in addition to the usual operations of addition and multiplication. In other words, the Lie bracket of any two dynamical functions is a dynamical function belonging to the same set $\mathcal{D}$. It is said that the set $\mathcal{D}$ of all dynamical functions has the structure of a *Lie algebra*.

The basic dynamical quantities have the following (postulated) properties:

$$
[q_j, p_n]_P = \delta_{j,n}, \quad [q_j, q_n]_P = [p_j, p_n]_P = 0. \quad (2.16)
$$

Clearly, when $b = q_j$ or $b = p_j$ Eq. (2.14) reduces to (2.12): Eq. (2.14) is therefore the most general form of the law of evolution. It is sometimes useful to write the latter equation in the form:

$$\partial_t b(q, p; t) = [H] \, b(q, p; t), \tag{2.17}$$

where the operator $[H]$ is defined as follows:

$$[H] = \sum_{j=1}^{F} \left\{ \frac{\partial H}{\partial p_j} \frac{\partial}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial}{\partial p_j} \right\}. \tag{2.18}$$

Eq. (2.17) can be *formally* solved [writing $b(q, p; t) \equiv b(t)$, $b(q, p; t = 0) \equiv b$]:

$$b(t) = \sum_n \frac{1}{n!} t^n b^{(n)}(0) = \sum_n \frac{1}{n!} t^n \, [H]^n \, b$$

hence:

$$b(t) = e^{[H] t} \, b \tag{2.19}$$

The operator $e^{[H] t}$ applied to the initial condition produces the value of the dynamical function at time t: it is called the *Propagator*. It can be shown that, as a result of the properties of the Lie bracket, the propagator acts on the dynamical functions in the following way:

$$b(q, p; t) = e^{[H] t} b(q, p; 0) = b \left(e^{[H] t} q, \, e^{[H] t} p; \, 0 \right) = b(q(t), p(t); 0) \tag{2.20}$$

The propagator acting on a scalar leaves the latter unchanged.

In order to illustrate the concepts introduced here, we consider a simple, but important question: What is the microscopic dynamical function describing the *mass density* of the system under consideration? Macroscopically, this quantity is represented by a *continuous* function $\rho(\mathbf{x}, t)$ [see Eq. (2.1)] defined as the limiting value of the ratio between the mass of matter contained in a region surrounding the point $\mathbf{x}$ in physical space, divided by the volume of that region, when the volume of this region shrinks to zero. In the microscopic picture, matter is composed of *discrete* massive point particles immersed in a vacuum. The definition given above therefore yields a zero value for the density at each point $\mathbf{x}$ in which there is no particle, and yields infinity at each point occupied by a particle. As the integral over the whole space must equal the finite value of the total mass, the singularity is a delta-function. By "testing" in this way every particle and adding up their partial contributions, we arrive at the definition for the mass density at point $\mathbf{x}$ and at a fixed time, say, $t = 0$:

$$\rho(q, p; \mathbf{x}, 0) = \sum_{j=1}^{N} m \, \delta \left(\mathbf{q}_j - \mathbf{x} \right) \tag{2.21}$$

The highly singular character of this dynamical function strikingly exhibits the contrast between the continuous macroscopic description and the discrete microscopic

picture of matter. In order to obtain the value of the density at an arbitrary time t, we apply the propagator to the dynamical function in the right hand side and use Eq. (2.20):

$$\rho(q, p; \mathbf{x}, t) = e^{[H] t} \sum_{j=1}^{N} m \, \delta \left(\mathbf{q}_j - \mathbf{x} \right) = \sum_{j=1}^{N} m \, \delta \left(\mathbf{q}_j(t) - \mathbf{x} \right) \qquad (2.22)$$

Note that the coordinate $\mathbf{x}$ of a point in physical space is a scalar from the point of view of phase space, whereas the coordinate of a particle $\mathbf{q}_j$ is a dynamical quantity: the propagator thus only acts on the latter.

Before closing this section, we emphasize again the *formal* character of the solution (2.19). We have not said anything about the nature of the functions appearing as solutions of the equations of motion. It turns out that these functions are, in general, extremely irregular, even for simple systems. This has been known since the beginning of this century (Poincaré), and has been the subject of an enormous amount of work in the last thirty years. The question is related to the concepts of ergodicity and deterministic chaos, which will be further discussed in Chap. 15. Eq. (2.19) must be understood in the following sense. Given an initial condition, the first order differential equation of motion possesses a unique solution represented by Eq. (2.19). The latter cannot be used in general as a practical means for calculating the solution for any finite time, because of the complicated nature of the solution space and of the extreme sensitivity to the initial conditions that characterizes a chaotic dynamical system. The symbolic notation for the solution of the equation of motion turns out, however, to be useful for our purpose.

2.4 Systems of Interacting Particles

Most problems discussed in this book relate to a collection of interacting particles (molecules, atoms, ions, electrons,...). We discuss here the generic form of the Hamiltonian of these systems: the equations obtained here will be used throughout the book.

We first consider a set of N *identical point particles*, each of mass m, in absence of an external field. Their Hamiltonian can then be written in the following form:

$$H = H^0 + H'. \qquad (2.23)$$

The term H^0 determines the *free motion* of noninteracting particles in the absence of an external field: it is simply the kinetic energy. It has the important property of being a sum of N terms, each depending only on the momentum of a single particle:

$$H^0 = \sum_{j=1}^{N} H_j^0, \tag{2.24}$$

with:

$$H_j^0 = \frac{p_j^2}{2m} . \tag{2.25}$$

The term H' represents the *interactions* between the particles. In most cases of interest, it can be written as a double sum of terms, each depending non-additively on the canonical variables of two particles:

$$H' = \sum_{j<}^{N} \sum_{n=1} V_{jn}. \tag{2.26}$$

V_{jn} is the potential energy of interaction between particles i and j, or, briefly, the *interaction potential;* the force exerted on particle j by particle n is: $\mathbf{F}_{jn} = -(\partial V_{jn}/\partial \mathbf{q}_j)$. The form (2.26) implies that this force is the same whether the two particles are isolated or are surrounded by other particles. This is not always true, but represents a quite good approximation in a very large number of important physical systems.

In many cases, we can further restrict the form of the interaction potential. In a non-relativistic theory, the real function V_{jn} usually depends only on the positions $\mathbf{q}_j$ and $\mathbf{q}_n$, not on the momenta. Moreover, it actually depends only on the distance $\mathbf{r}_{jn} = \mathbf{q}_j - \mathbf{q}_n$, and more specifically on the absolute value of this vector: $|\mathbf{r}_{jn}| \equiv r_{jn}$:

$$V_{jn} = V\left(|\mathbf{q}_j - \mathbf{q}_n|\right) = V\left(r_{jn}\right). \tag{2.27}$$

As the particles are identical, each term V_{jn} in Eq. (2.26) represents the *same function* of the variable r_{jn} pertaining to the couple jn. The form (2.27) has the obvious symmetry consequence:

$$V_{jn} = V_{nj} . \tag{2.28}$$

Moreover, we note the important property:

$$\frac{\partial V_{jn}}{\partial \mathbf{q}_j} = -\frac{\partial V_{jn}}{\partial \mathbf{q}_n} . \tag{2.29}$$

This equality is the expression of Newton's third law (action = reaction).

In some cases it is useful to work with the Fourier transform of the interaction potential. This function is defined as usual by the two mutually inverse equations:

$$V(r) = \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, \widetilde{V}(\mathbf{k}) , \tag{2.30}$$

$$\tilde{V}(\mathbf{k}) = (2\pi)^{-3} \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, V(r) \,. \tag{2.31}$$

It is readily checked that the form (2.27) implies that $\tilde{V}(\mathbf{k})$ is a real function of the absolute value k of the vector $\mathbf{k}$:

$$\tilde{V}(\mathbf{k}) = \tilde{V}(-\mathbf{k}) = \tilde{V}(k). \tag{2.32}$$

The form of the interaction potential depends, of course, on the nature of the particles. For charged particles (whose charge is e) it is the *Coulomb potential*:

$$V^{C}(r) = \frac{e^2}{r} \,; \tag{2.33}$$

for neutral particles it is usually taken to be the *Lennard-Jones potential*:

$$V^{LJ}(r) = V_0 \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6} \right] \,. \tag{2.34}$$

The latter potential, shown in Fig. 2.1, depends on two characteristic parameters. V_0 characterizes the maximum strength of the attractive interactions and r_0 (position of the minimum) can be related to the range of the interactions. We also note the presence of a hard core: as $r \to 0$, the interaction becomes repulsive and tends to infinity.
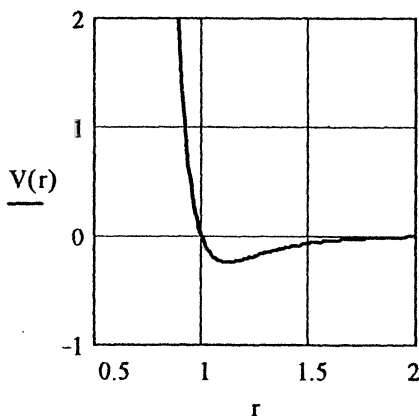
Figure 2.1: The Lennard-Jones potential in reduced units ($V_0 = 1$, $r_0 = 1$).
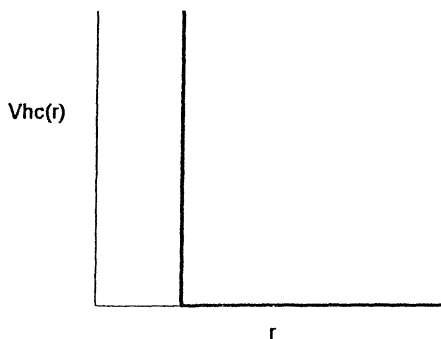
Figure 2.2: The hard sphere potential.

When the attractive part of the interaction is very small, one often uses the simple model of *hard spheres* to represent spherical particles of diameter r_0 that move freely in space, except for encounters at a distance r_0, which result in an elastic collision (see Fig. 2.2).

This potential has no parameter characteristic of strength: the latter is either zero or infinity:

$$V^{HS}(r) = \begin{cases} \infty, & r < r_0 \\ 0, & r > r_0 \end{cases} \tag{2.35}$$

The Coulomb potential (2.33), on the other hand, lacks a parameter measuring the range (the coupling strength is measured by a parameter proportional to the square of the charge). The Coulomb potential decreases *very slowly* to zero ("very slowly" implies, in particular, that many integrals involving $V(r)$ diverge, as is well known already from equilibrium statistical mechanics): it is said that this potential has a *"long tail"*, or that its interaction range is infinite (see Fig. 2.3).

It is, however, well known from equilibrium theory that in a plasma or in an electrolyte, the interaction between two given particles is actually *screened* by the presence of the other particles (that have charges of both signs): as a result, the effective interaction in a plasma is described (in first approximation) by a *Debye potential* (Fig. 2.3):

$$V^D(r) = e^2 \frac{\exp(-r/r_D)}{r} . \tag{2.36}$$

This potential possesses a characteristic range parameter, the Debye length r_D.
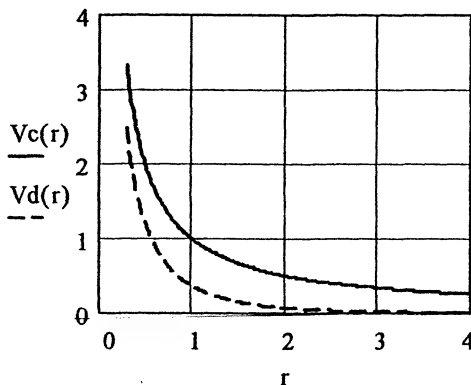
Figure 2.3: The Coulomb potential (solid) and the Debye potential (dashed) in re-duced units $(e = 1, \ r_D = 1)$.

Contrary to the parameters r_0 appearing in previous formulae, r_D is not an intrinsic property of the particles, but rather a collective feature depending on the macroscopic state of the system: number density n and temperature T $(k_B$ is the well-known Boltzmann constant):

$$r_D = \left(\frac{4\pi e^2 n}{k_B T}\right)^{-1/2} . \tag{2.37}$$

The problem of the screening, in particular the screening process in non-equilibrium situations, will be further discussed in Chaps. 5 and 8.

We now briefly consider the case in which an *external field* is present. This field introduces an additional term H^F in the Hamiltonian. For a gravitational or an electrostatic field, the force derives from a potential function $V^F(\mathbf{x};t)$ which may depend on time. The contribution to the Hamiltonian is then simply:

$$H^F = \sum_{j=1}^{N} V^F(\mathbf{q}_j;t) . \tag{2.38}$$

This term has the same structure as H^0, Eq. (2.24): a sum of terms depending on the coordinates of a single particle, but also (generally) on time.

2.5   Bibliographical Notes BN2

Among the many books treating the hydrodynamical equations, we single out the following ones, which are particularly well adapted for physicists:

Landau, L.D. and Lifshitz, E.M., 1987, *Fluid Mechanics*, 3rd English edition, Butterworth-Heinemann, Oxford

de Groot, S.R. and Mazur, P., 1969, *Nonequilibrium Thermodynamics*, 2nd edition, North Holland, Amsterdam

The best exposition of classical mechanics for physicists, and in particular, Hamiltonian dynamics, remains:

H. Goldstein, 1980, *Classical Mechanics*, (2nd. ed.), Addison-Wesley, Cambridge, Mass.

A more elementary introduction, remarkably modern and well written is:

Percival, I. and Richards, D., 1982, *Introduction to Dynamics*, Cambridge Univ. Press.

A more mathematical, but very clear and readable text is:

Arnold, V.I., 1979, *Mathematical Methods of Classical Mechanics*, Springer, Berlin

A very important review paper on Hamiltonian dynamics, with an opening toward relativity, is:

Dirac, P.A.M., 1949, Rev. Mod. Phys., **21**, 392.

The algebraic (and group-theoretical) approach of this paper inspired us in several works, as well as in the presentation given in **RB-2**, and, more briefly, here. This same philosophy is amply expanded in the following excellent book:

Sudarshan, E.C.G. and Mukunda, N., 1983, *Classical Dynamics: A Modern Perspective*, Krieger, Malabar, Florida.

Chapter 3

General Formalism of Statistical Mechanics

3.1 Macroscopic Physics and Microscopic Physics

The objects of macroscopic physics, i.e., the objects that can be directly perceived at our human level, are naturally inscribed in a euclidian three-dimensional space; their evolution introduces an aditional, fourth dimension: time.Thus, these objects are naturally modelled mathematically as *continuous functions* (or piecewise continuous functions) of three spatial coordinates $x = (x_1, x_2, x_3)$ and time t, i.e., as *fields*: $B(x,t)$ [see Sec. 2.2]. As a result, the great disciplines of macroscopic physics, such as fluid mechanics, elasticity, acoustics, electromagnetism, are field theories. These fields are determined by partial differential equations, or integro-differential equations, involving unknown functions of time and of the three coordinates $x = (x_1, x_2, x_3)$ of the *physical space*.

. This view of physics was deeply altered in the second half of the 19-th century, after the beginnings and the confirmation of the atomistic theories. The resulting idea was that the view of matter and energy as a continuum is but an illusion. If matter could be looked at on a scale length of about 10^{-7} *cm* one would only see a collection of an immense number of *discrete particles*. It may be noted that since about 1980 the last doubts (if there were any left!) about the reality of the atoms have been lifted. The discovery of the tunnel effect microscope allowed one not only to see the atoms on the surface of a solid, but even to manipulate them, i.e., pick them up, individually, and displace them to another position! The natural description of such a system is in terms of *dynamics of a system of N particles,* each one of these being idealized as a point particle, or as a small system with few degrees of freedom. It is important that N be a VERY LARGE number. The evolution in time of this system is fundamentally determined by the laws of quantum mechanics, but in many cases classical mechanics

is a sufficient approximation.

The microscopic and the macroscopic descriptions of the phenomena are, in principle, equivalent descriptions of the same reality. Nevertheless, the form of the laws derived at these two levels are so different from each other that there soon appeared a stringent need for an explanation of the laws of continuum physics in terms of the microscopic evolution of the underlying collection of atoms. This bridge between the two levels of description is provided by STATISTICAL MECHANICS.

The description of a piece of matter in terms of the positions and momenta of each individual atom at every time is clearly much too detailed. A macroscopic observer can never prepare a system according to such a specification. On the other hand, even if an ideal computer existed that could solve the initial value problem for a system of 10^{23} particles, the knowledge of the position of each particle at all times would not help us at all in solving a problem of hydrodynamics. It should be realized that the specific feature of statistical mechanics is NOT that of being a "super-mechanics"; rather, in this science *the questions asked about the many-body system are different from those asked about the motion of individual atoms.*

In order to illustrate our point, we discuss the following simple experiment. The system under consideration is a metal rod. At time $t = 0$, its temperature varies linearly from a high value T_H at its left end to a low value T_L at the right end. At later times, the system is left to evolve freely and the temperature is measured as a function of time at several points along the rod. Macroscopic physics (i.e., the heat equation) predicts an evolution of the temperature towards a homogeneous distribution for long enough time, and this prediction is very accurately verified by the actual measurements.

This experiment can be repeated many times with the same macroscopic preparation: the results are perfectly reproducible. But in each new realization the positions and the momenta of the atoms at time zero will be different: the mere specification of a macroscopic temperature profile is by far insufficient for a complete specification of the initial data of all the particles. In other words, there are *many different initial molecular configurations* that are compatible with our limited macroscopic specification. Nevertheless, the experimental evidence shows that the macroscopic evolution is insensitive to these different microscopic configurations. Hence the idea that all different microscopic configurations compatible with the macroscopic constraint are equivalent, and should be treated on the same footing. One way of realizing this idea mathematically is to attach a certain *weight* to all possible configurations at time zero. For instance, one would attach a weight 0 to all states that are incompatible with the given constraint, and an equal, non-zero weight to all states that are compatible with it. We are then tempted to define any observable macroscopic dynamical quantity as the *average* of the corresponding microscopic dynamical quantity over *all* states of the system, properly weighted as described. By this procedure, it is clear

that, starting the system in any configuration compatible with the macroscopic constraint results in equal values of the macroscopic quantities: we have an explanation of the reproducibility of the macroscopic experiments. The discussion given above was done in the classical description. The same ideas are, however, valid in quantum mechanics, which has already a statistical aspect in its very essence. As explained in the introduction, however, we do not treat here quantum statistical mechanics.

We thus arrive at the idea of a *statistical description* of the many-body system. The mathematical object representing the state of the system is no longer a point in phase space, but rather a collection of points, each one being weighted by a certain number. Such a set of weighted points will be called an ENSEMBLE. The observable value of a dynamical function is identified with the ensemble average of the microscopic dynamical function. The value obtained in this way is interpreted as *the average outcome of a large number of identical experiments*. The value of a specific individual experiment cannot be predicted: there always exist *fluctuations* around the average (which can be described statistically by the formalism). But, if the system is large enough, the relative value of the fluctuations becomes negligibly small[1], and the ensemble average yields a quite accurate prediction of individual experiments.

3.2   The Phase Space Distribution Function

We now formalize the concepts introduced qualitatively in the previous paragraph. We consider a conservative dynamical system having F degrees of freedom, described in classical Hamiltonian dynamics by a set of position coordinates $q \equiv (q_1, ..., q_F)$ and the corresponding momenta $p \equiv (p_1, ..., p_F)$ [see Eq. (2.11)]. (For definiteness, we may think of a system of N point particles, in which case $F = 3N$). The motion is generated by a Hamiltonian $H(q, p)$.

The objects of macroscopic physics are represented by continuous functions in physical space: they are *fields*: $B(\mathbf{x}, t)$. The corresponding microscopic dynamical quantities, in the classical mechanical description, are *functions of the phase space variables* which may also depend on the *parameters* $\mathbf{x}, t$ (which are "scalars" in phase space): $b(q, p; \mathbf{x}, t)$ [see the example of the mass density described in Sec. 2.3]. The purpose of statistical mechanics is to create a bridge between the two worlds, by associating with each microscopic dynamical function a unique macroscopic quantity:

$$b(q, p; \mathbf{x}, t) \rightarrow B(\mathbf{x}, t). \qquad (3.1)$$

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[1]This statement applies to the fluctuations of global quantities (such as the total energy, or the total number of particles). Local fluctuations of intensive quantities (pressure, density, velocity, electric or magnetic fields) are small but not negligible. They play an essential role in certain phenomena (such as anomalous or strange transport) that will be treated in forthcoming chapters of this book (Chaps. 11 - 14).

This correspondence (3.1) defines *a* mapping of the phase space on the physical space. In order to define this mapping more precisely, we require a few natural conditions.

The correspondence is, technically speaking, a *functional:* for given $\mathbf{x}, t$, with each choice of a *function* of q, p it associates a *number.* This functional will be denoted by the following equivalent notations:

$$B(\mathbf{x}, t) \equiv \langle b(q, p; \mathbf{x}, t) \rangle \equiv \langle b \rangle. \tag{3.2}$$

A) It is required that a phase space scalar β be unaffected by the mapping;

$$\langle \beta \rangle = \beta; \tag{3.3}$$

in particular, for the constant 1 we have:

$$\langle 1 \rangle = 1. \tag{3.4}$$

B) It is required that the *functional be linear:* if b and c are two dynamical functions, and β, γ are two scalars, the following relation should hold:

$$\langle \beta b + \gamma c \rangle = \beta \langle b \rangle + \gamma \langle c \rangle. \tag{3.5}$$

It is easy to construct a realization of this functional involving the characteristic objects of the classical phase space. Let $F(q, p)$ be a phase space function, chosen once for all, and consider the expression:

$$B(\mathbf{x}, t) \equiv \langle b \rangle = \int dq \, dp \, b(q, p; \mathbf{x}, t) \, F(q, p). \tag{3.6}$$

The integration sign actually denotes a multiple integral over the whole phase space domain accessible to the system (typically, the q-integrations extend over the interior of the box containing the system, and the p-integrals extend from $-\infty$ to $+\infty$). The integral in Eq. (3.6) associates with every function $b(q, p; \mathbf{x}, t)$ a number $B(\mathbf{x}, t)$ depending on the physical space coordinates and on time, as described in Eq. (3.1): it thus defines a functional. Obviously, this functional possesses the property (3.5). We now restrict the choice of the functions $F(q, p)$ by imposing the *normalization condition:*

$$\int dq \, dp \, F(q, p) = 1. \tag{3.7}$$

As a result, the condition (3.4) is then also satisfied. We moreover require the functions $F(q, p)$ to be *positive definite* (this additional condition is not logically necessary, but it gives a clear physical meaning to the function F, see below):

$$F(q,p) \geq 0, \qquad \forall q,p. \tag{3.8}$$

The functions $F(q,p)$ satisfying Eqs. (3.7), (3.8) form a subset of the set of dynamical functions. These functions will be called PHASE SPACE DISTRIBUTION FUNCTIONS (or simply: DISTRIBUTION FUNCTIONS). We now formulate the *basic postulate of classical statistical mechanics:*

The STATE *of a system is completely specified, in the framework of classical statistical mechanics, by the specification of a phase space distribution function $F(q,p)$ satisfying Eqs. (3.7), (3.8). The* OBSERVABLE *(macroscopic) value of a dynamical function $b(q,p;\mathbf{x},t)$ is the field $B(\mathbf{x},t)$ defined by Eq. (3.6).*

The functions $F(q,p)$ possess all the necessary properties (positive definite character, normalization to unity) allowing us to interpret them as phase space *probability densities.* Explicitly, $F(q,p)\,dq\,dp$ is interpreted as the probability of finding the system within the infinitesimal domain $(q,q+dq),(p,p+dp)$ in phase space. The dynamical function b no longer has a definite value in the new perspective: rather, it may have any one of the possible values taken by the function $b(q,p;\mathbf{x},t)$ when (q,p) sweeps over the whole phase space (for fixed $\mathbf{x},t$). In other words, it is considered as a *random function.* Eq. (3.6) is then simply the usual presciption for calculating the average value (or expectation value) of the random function $b(q,p;\mathbf{x},t)$. The functional (3.6) will therefore be called the *phase space average of the dynamical quantity* $b(q,p;\mathbf{x},t)$.

The description of the dynamical system in the framework of classical statistical mechanics is thus radically different from the one of ordinary classical mechanics. The state of the system is no longer represented by a point in phase space. *All* points of phase space are *possible* states of the system, each one of them being *weighted* by the value of the distribution function in that point. We thus recovered the idea of a STATISTICAL ENSEMBLE discussed in Sec. 3.1. At this stage we see what was meant there by saying that "the questions asked about a many-body system are different in statistical mechanics". We do not require the knowledge of the instantaneous position of the system in phase space (the system can be *anywhere* at each time), but rather the specification of the probability density of presence at any phase space point.

The realization of the prescription (3.6) requires the choice of a distribution function $F(q,p)$ [2]. This is a *non-mechanical problem.* The choice of the distribution function representing the best of our knowledge about the system represents the specifically *statistical* aspect of statistical mechanics. In "orthodox" statistical mechanics, which is under discussion here, we impose the following rule: Once a distribution function $F(q,p)$ is chosen, *the subsequent evolution of the system is strictly determined by the*

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[2]This choice has the same status as the specification of an initial condition for a differential equation; see below.

laws of classical mechanics. This is a very stringent constraint, which is, however, necessary for a rigorous foundation of statistical mechanics. It will raise the difficult "irreversibility paradox" mentioned in Sec. 2.2.

We now determine the law of evolution of the macroscopic quantity $B(\mathbf{x}, t)$, i.e., the phase space average of the microscopic dynamical quantity $b(q, p; \mathbf{x}, t)$. We assume that initially (at time $t = 0$):

$$b(q, p; \mathbf{x}, t = 0) = b(q, p; \mathbf{x}), \tag{3.9}$$

where the right hand side is a given function. Then, at time zero:

$$B(\mathbf{x}, 0) = \int dq\, dp\, b(q, p; \mathbf{x})\, F(q, p). \tag{3.10}$$

When the microscopic system evolves according to Hamiltonian dynamics, the quantity $b(q, p; \mathbf{x})$ becomes at time t the quantity $b(q, p; \mathbf{x}, t)$ determined by Eq. (2.19). The phase space average of this new dynamical quantity is:

$$B(\mathbf{x}, t) = \int dq\, dp \left\{ e^{[H]\, t} b(q, p; \mathbf{x}) \right\} F(q, p). \tag{3.11}$$

This equation defines the *law of evolution of the macroscopic quantities in physical space as induced by the Hamiltonian dynamics in phase space.* It suggests an analogy with the "Heisenberg representation" of quantum mechanics: in the averaging process the state of the system is kept fixed, whereas the dynamical quantities evolve in time.

At this point there appears a difficulty. In order to apply the prescription (3.11) a separate differential equation must be solved in order to determine each time-dependent dynamical function $b(q, p; \mathbf{x}, t)$ whose average is being sought. We now show that the problem can be enormously simplified (in principle) by constructing an alternative (though equivalent) procedure by which it is sufficient to solve a single partial differential equation for a given dynamical system. When this solution is known, the evaluation of the phase space averages of all dynamical functions, at arbitrary times, reduces to "simple" quadratures. We first need a lemma.

If the same canonical transformation $e^{[G]\, r}$ (generated by the dynamical function G and parametrized by the parameter r) *is applied to both factors in the integrand of Eq. (3.6), the value of the integral is unchanged.*

The proof is based on an important property: A canonical transformation acting on a function $f(q, p)$ yields the original function of the transformed variables [see Eq. (2.20)]. Hence:

$$\int dq\, dp \left\{ e^{[G]r} b(q, p; \mathbf{x}, t) \right\} \left\{ e^{[G]r} F(q, p) \right\}$$

$$= \int dq\, dp\, b(q_r, p_r; \mathbf{x}, t)\, F(q_r, p_r) \tag{3.12}$$

where:

$$q_r = e^{[G]\,r}q, \quad p_r = e^{[G]\,r}p.$$

In the right hand side of (3.12) change the integration variables: $q \to q_r, \quad p \to p_r$:

$$\int dq\,dp\; b(q_r, p_r; \mathbf{x}, t)\, F(q_r, p_r) = \int dq_r\,dp_r\; |J|\, b(q_r, p_r; \mathbf{x}, t)\, F(q_r, p_r)$$

where J is the Jacobian of the transformation. But another important property of canonical transformations is: $J = 1$. The lemma is thus proved.

We now return to Eq. (3.11) and apply to both factors the canonical transformation inverse to $e^{[H]\,t}$: as a result of the previous lemma this operation does not change the value of the integral:

$$B(\mathbf{x}, t) = \int dq\,dp\, \left\{ e^{-[H]\,t}e^{[H]\,t}\, b(q, p; \mathbf{x}) \right\} \left\{ e^{-[H]\,t}\, F(q, p) \right\}.$$

The two successive transformations in the first bracket cancel each other: the whole time dependence is thus "transferred" to the distribution function. It is thus quite natural to define a *time dependent distribution function*:

$$F(q, p; t) = e^{-[H]\,t}\, F(q, p). \tag{3.13}$$

In terms of this function, the phase space average at time t is defined by:

$$B(\mathbf{x}, t) = \int dq\,dp\, b(q, p; \mathbf{x})\, F(q, p; t). \tag{3.14}$$

In this new "Schrödinger picture" the time dependence is entirely contained in the function $F(q, p; t)$: if this single function is known, the calculation of all the macroscopic (time-dependent) quantities is reduced to quadratures involving time-independent dynamical quantities $b(q, p; \mathbf{x})$. As stated above, it is no longer necessary to solve a separate equation of motion for each dynamical function. The determination of the time-dependent distribution function requires the solution of a partial differential equation obtained from Eq. (3.13):

$$\partial_t F(q, p; t) = [H(q, p),\, F(q, p; t)]_P. \tag{3.15}$$

(Note the order of the factors in the Poisson bracket!) Eq. (3.15) is called the LIOUVILLE EQUATION: it is the basic equation of classical statistical mechanics.

An important property of the Liouville equation is its linearity. In order to stress this fact, it is convenient to use also an alternative notation for this equation:

$$\partial_t F(q, p; t) = L F(q, p; t). \tag{3.16}$$

The linear operator L, called the LIOUVILLIAN, is defined as follows:

$$LF \equiv [H, F]_P = \sum_{j=1}^{3N} \left\{ \frac{\partial H}{\partial q_j} \frac{\partial F}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial F}{\partial q_j} \right\}. \tag{3.17}$$

(where N is the number of particles). Eq. (3.16) is a linear first order partial differential equation. It is well known that the solution of such an equation is given as a general function of its first integrals, obtained by solving the associated characteristic equations. It is immediately seen that the latter are nothing other than Hamilton's equations (2.12): this proves once more that the temporal evolution in statistical mechanics is (at its starting point) exactly determined by the laws of classical mechanics. More precisely, the solution of the initial value problem can be written by making Eq. (3.13) explicit. Comparing it to Eq. (2.20) which determines the formal solution for the dynamical quantities, one should take care of the minus sign in the exponential of the former: this corresponds to solving the equation of motion backward in time. The solution of the Liouville equation is thus rewritten as:

$$F(q, p; t) = F(q(-t), p(-t); 0), \tag{3.18}$$

where $q(-t)$ denotes the value of the position at time $-t$, given the initial value q at time zero (and a similar definition for $p(-t)$). It should be clear from the beginning that q, p denote the set of phase space coordinates of the dynamical system, whereas $q(-t), p(-t)$ are dynamical functions of q and p.

The Liouvillian plays in statistical mechanics the same role as the Hamiltonian in ordinary mechanics: it is the generator of the evolution. But instead of acting on a point in phase space, it acts on the distribution function.

We now write down the explicit expression of the Liouvillian for our standard Hamiltonian of a set of N interacting particles (2.23)-(2.27). We introduce the *velocity* of particle j:

$$\mathbf{v}_j = \frac{\mathbf{p}_j}{m}, \tag{3.19}$$

and use the following abbreviations:

$$\nabla_j \equiv \frac{\partial}{\partial \mathbf{q}_j}, \quad \partial_j \equiv \frac{\partial}{\partial \mathbf{p}_j}, \quad \partial_{jn} \equiv \partial_j - \partial_n. \tag{3.20}$$

As a result of the linearity, the Liouvillian has the following form:

$$L = L^0 + L' = \sum_{j=1}^{N} L_j^0 + \sum_{j<}^{N} \sum_{n=1}^{N} L'_{jn}, \tag{3.21}$$

with:

$$L_j^0 = -\mathbf{v}_j \cdot \nabla_j \, , \tag{3.22}$$

$$L'_{jn} = (\nabla_j V_{jn}) \cdot \partial_{jn} \tag{3.23}$$

In deriving this last result we made use of the property (2.29).

If an external field is present, the Liouvillian contains an additional contribution that is easily derived from Eq. (2.38):

$$L^F = \sum_{j=1}^N L_j^F = \sum_{j=1}^N \left(\nabla_j V_j^F\right) \cdot \partial_j \tag{3.24}$$

~~Before closing this section, we introduce an important warning. Eq. (3.6) defines~~ a functional, i.e. a mapping of the phase space on the physical space:

$$b(q,p) \to B.$$

As a result: *to each dynamical function $b(q,p)$ corresponds one single macroscopic observable B.* One is tempted to reciprocate: "to each macroscopic observable corresponds a single microscopic dynamical function $b(q,p)$". The latter statement is *wrong*. It is well known from equilibrium statistical mechanics (see next section) that there exist important thermodynamical quantities (such as: temperature, entropy,...) that are not of the form (3.6) . We may thus define two classes of macroscopic functions: *mechanical quantities*, which are of the form (3.6), and *thermal quantities* that are not of this form. The latter quantities are of a global nature, they are properties of the state of the system, hence of the distribution function.

3.3 Equilibrium States

The Liouville equation (3.15) is an extraordinarily complicated equation for a function of $3N + 1$ variables: it cannot be solved analytically in any non-trivial situation. We may, however, ask what are the special solutions $F^0(q,p)$ of this equation that are independent of time (i.e., the *stationary solutions*). This particular problem is trivially simple. Indeed, the Liouville equation then reduces to:

$$\left[H(q,p), F^0(q,p)\right]_P = 0. \tag{3.25}$$

Without any calculation, a first solution is found simply by using the algebraic properties (2.15), in particular the antisymmetry of the Poisson bracket: the bracket of any function with itself is identically zero. Hence the Hamiltonian H is a particular solution, but it is, in general, neither normalized, nor definite positive. But any function of H is also a solution, hence the physically acceptable solutions are:

$$F^0(q,p) = \Phi[H(q,p)], \tag{3.26}$$

where Φ is *any function of the Hamiltonian which [regarded as a function of (q,p)] satisfies the conditions (3.7), (3.8)*.[3]

We have thus obtained the general solution of the stationary Liouville equation without any effort. But we are left with an enormous amount of arbitrariness. As noted in Sec. 3.2, the choice of a specific function $\Phi(H)$ is no longer a dynamical problem, but rather a statistical one. This leads us to the foundations of *Equilibrium statistical mechanics*, which we only very briefly summarize here, because the reader is supposed to be at least weakly acquainted with this field (see references in **BN3**).

The choice is based on a very natural statistical principle, called the *principle of equal a priori probabilities*: it was used implicitly by Gibbs, but was clearly formulated by Tolman in 1938. Whatever is known about the system by a macroscopic observer is expressed as a constraint, limiting the accessible part of the phase space. Once all the constraints are expressed, all states in this accessible region must be given equal probabilities: indeed, we have no single element allowing us to distinguish one state from another.

The most direct application of this principle is to an *isolated system*. In this case the distribution function must be uniform on an energy surface, and zero elsewhere. This defines the *microcanonical ensemble*, which is an important theoretical tool, but not a practical one, because of its singular nature. The most important equilibrium ensemble is the one describing a *closed system*, which can exchange energy with the external world (which is supposed to be globally isolated). An appropriate application of the principle of equal a priori probabilities to this case [see **RB-2**] leads to the *canonical ensemble*, characterized by the folowing distribution function:

$$F^0(q,p) = \frac{1}{h^{3N}\,N!\,Z(T,V,N)}\,\exp\left[-\frac{H(q,p)}{k_B\,T}\right]. \tag{3.27}$$

As required by Eq. (3.26) the dependence on the phase space variables enters only through the Hamiltonian. The factors $h^{3N}\,N!$ (where h is Planck's constant)

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[3]It would seem that (3.26) is only a particular class of solutions. A "general" solution would be a function of all the integrals of the motion, $I_n(q,p)$: these are precisely defined by the relation $[H, I_n]_P = 0$. It turns out, however, that for any system of interacting particles (which is globally at rest with respect to the observer), all integrals of the motion, but for the Hamiltonian, are "non-isolating functions". Whereas the motion of a system with a given value of the Hamiltonian is restricted to a hypersurface (the energy surface) of dimension $(3N - 1)$ in phase space, there exist no such hypersurfaces associated with the other integrals of the motion: if one tried to construct one, he would find that its intersection with the energy surface passes arbitrarily close to every point of the latter. In other words, the orbit of the system covers densely the energy surface. This is a particular (and highly simplified) form of the ergodic theorem. In this form it was first established by Poincaré. It is also closely related to the so-called "integrability problem" of the nonlinear differential equations. This problem will be further discussed in Chap. 15.

are required for consistency with the quantum mechanical result; V is the volume. A discussion of the thermodynamical implications of the canonical ensemble leads to the interpretation of T as the absolute temperature and of k_B as the Boltzmann constant. The quantity $Z(T, V, N)$, called the PARTITION FUNCTION, plays a central role in equilibrium statistical mechanics: it is essentially the normalization constant of the distribution function (3.27):

$$Z(T, V, N) = \frac{1}{h^{3N} N!} \int dq \, dp \, \exp\left[-\frac{H(q,p)}{k_B T}\right].$$ (3.28)

where the integration is over the whole accessible phase space, i.e. over the whole volume V for each q_j and from $-\infty$ to ∞ for each p_j. The partition function is thus a functional of the Hamiltonian; after the integrations it depends on the three parameters T (temperature), V (volume) and N (number of particles). The thermodynamical discussion which led to the interpretation of T as the temperature also leads to the following *fundamental relation of equilibrium statistical mechanics:*

$$A(T, V, N) = -k_B T \, \ln Z(T, V, N).$$ (3.29)

This equation relates the partition function to the *Helmholtz free energy* $A(T, V, N)$. Its importance lies in the fact that $A(T, V, N)$ is a *thermodynamic potential*: if it is known as a function of the variables (T, V, N), all other thermodynamic quantities can be calculated by simple differential formulae; for instance, the pressure $P(T, V, N)$ and the entropy $S(T, V, N)$ are obtained as follows:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N},$$ (3.30)

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}.$$ (3.31)

A first important aspect is that all *thermal quantities* mentioned in the previous section (i.e., quantities that cannot be expressed as averages of microscopic dynamical functions) are now defined (at least, in equilibrium). Thus, the temperature appears as a parameter characterizing the distribution function; the free energy and the entropy appear to be nonlinear functionals of the distribution function. All these aspects show that the thermal quantities are global properties characterizing the equilibrium state of the system.

In conclusion, once the partition function is calculated from Eq. (3.28), all thermodynamic quantities are obtained without a new appeal to microscopic physics. Thus, *Eq. (3.29) contains the complete solution of the problem of equilibrium statistical mechanics.* There exists, unfortunately, no such "magical" formula for nonequilibrium statistical mechanics!

The subsequent development of equilibrium statistical mechanics consists in designing approximation methods for the evaluation of the partition function, given the Hamiltonian, thus the molecular interaction potential, and the value of the thermodynamical variables (T, V, N). This poses in general a complicated (practical) problem. Among the very few cases where the problem can be evaluated analytically, we mention the (classical) ideal gas, i.e., a collection of non-interacting particles of mass m. Using Eqs. (2.23) - (2.25) with $H' = 0$, one easily obtains the canonical distribution function:

$$F^0(q, p) = \frac{1}{(2\pi m\, k_B T\, V)^N} \exp\left[-\frac{1}{k_B T} \sum_{j=1}^{N} \frac{p_j^2}{2m}\right]. \tag{3.32}$$

In all other cases, some more or less drastic approximations must be applied: these constitute the field of equilibrium statistical mechanics!. Some problems have resisted for a long time, but have finally yielded. Among these recent successes we should mention the beginning of our understanding of the mysterious critical phenomena: these will be discussed in Chaps. 13 and 14.

3.4 Bibliographical Notes BN3

The fundamental work mentioned in Sec. 2.2 is:

H. Poincaré, 1892, *Méthodes Nouvelles de Mécanique Céleste*, (3 vols.), Gauthier-Villars, Paris; reprinted by: Libr. Sc. Techn. A. Blanchard, Paris, 1987;   english translation: H. P., *New Methods of Celestial Mechanics*, AIP Press, Williston, Vermont

We now give a list of textbooks or monographs on statistical mechanics. Although rather long, it does not claim completeness. For convenience, we present three groups.In a first group we list· rather old works, which have acquired a "historical" interest and still remain important references. In a second and third groups we list books published since 1975 (an arbitrary origin!). In the second group we list books treating *only* equilibrium theory; in the third we quote books including at least one chapter on some non-equilibrium problems (most often, the non-equilibrium part is very small!)

1. "Historical" references.

Gibbs, J.W., 1902, *Elementary Principles in Statistical Mechanics*, Yale Univ. Press, N.H. (reprinted by Dover, N.Y., 1960)

Fowler, R.H., 1936, *Statistical Mechanics*, Cambridge Univ. Press, Cambridge

Tolman, R.C., 1938, *Statistical Mechanics,* Clarendon Press, Oxford,

Mayer, J. and Mayer, M.G., 1940, *Statistical Mechanics,* Wiley, New York,

Schrödinger, E., 1948, *Statistical Thermodynamics,* Cambridge Univ. Press, Cambridge

Khinchine, A.I., 1949, *Mathematical Foundations of Statistical Mechanics,* Dover, New York,

Hill, T.L., 1956, *Statistical Mechanics,* McGraw Hill, New York,

Prigogine, I., 1963, *Non-Equilibrium Statistical Mechanics,* Interscience, New York,

Sommerfeld, A., 1964, *Lectures in Theoretical Physics,* vol.5: *Thermodynamics and Statistical Mechanics,* Academic Press, New York,

Münster, A., 1969, *Statistical Thermodynamics,* Springer, Berlin and Academic Press, New York,

Ruelle, D., 1969, *Statistical Mechanics, Rigorous Results,* Benjamin, New York.

2. Recent books dealing only with Equilibrium Statistical Mechanics.

Landau, L.D. and Lifshitz, E.M., 1980, *Statistical Physics,* (3rd. ed., reprint), Butterworth Heinemann, Oxford,

Mandl, F., 1988, *Statistical Physics,* 2d. ed., Wiley, New York,

Goodstein, D.L., 1985, *States of Matter,* (reprint), Dover, New York,

Plischke, M. and Bergersen, B., 1994, *Equilibrium Statistical Physics,* 2d. ed., World Scientific, Singapore,

Greiner, W., Neise, L. and Stöcker, H., 1995, *Thermodynamics and Statistical Mechanics,* Springer, Berlin,

Toda, M., Kubo, R., and Saitô, N., 1995, *Statistical Physics I: Equilibrium Statistical Mechanics,* (2d. ed., 2d. print.), Springer, Berlin.

3. Recent books containing at least one chapter on Non-equilibrium Statistical Mechanics.

Balescu, R., 1975, *Equilibrium and Nonequilibrium Statistical Mechanics,* (**RB-2**), Wiley, New York,

McQuarrie, D., 1976, *Statistical Mechanics,* Harper and Row, New York,

Lifshitz, E.M. and Pitaevskii, L.P., 1980, *Statistical Physics, Part 2,* (reprint), Butterworth Heinemann, Oxford,

Akhiezer, A.I. and Peletminsky, S.V., 1981, *Methods of Statistical Physics,* Pergamon, Oxford,

Kreuzer, H.J., 1981, *Nonequilibrium Thermodynamics and its Statistical Foundation,* Clarendon Press, Oxford,

Lifshitz, E.M. and Pitaevskii, L.P., 1981, *Physical Kinetics,* (reprint), Butterworth Heinemann, Oxford,

Ma, S.K., 1985, *Statistical Mechanics,* World Scientific, Singapore,

Klimontovich, Yu.L., 1986, *Statistical Physics,* Harwood Academic Publ., Chur,

Chandler, D., 1987, *Introduction to Modern Statistical Mechanics,* Oxford Univ. Press,

Huang,K., 1987, *Statistical Mechanics*, (2d. ed.), Wiley, New York,

Wannier, G.H., 1987, *Statistical Physics*, (reprint), Dover, New York,

Agarwal, B.K. and Eisner, M., 1988, *Statistical Mechanics*, Wiley, New York,

McLennan, J.A., 1989, *Introduction to Nonequilibrium Statistical Mechanics*, Prentice Hall, Englewood Cliffs, NJ,

Reichl, L., 1991, *A Modern Course in Statistical Physics*, Arnold, New York,

Spohn, H., 1991, *Large Scale Dynamics of Interacting Particles*, Springer, Berlin (this book is written with full mathematical rigour),

Vauclair, S., 1993, *Eléments de Physique Statistique*, InterEditions, Paris,

Kubo, R., Toda, M. and Hashitsume, N., 1995, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, (2d. ed., 2d. print.), Springer, Berlin,

ter Haar, D., 1995, *Elements of Statistical Mechanics*, (3rd. ed.), Butterworth Heinemann, Oxford.

All the recent books quoted above contain a thorough exposition of *quantum equilibrium statistical mechanics*. Some of them also contain a discussion of *quantum non-equilibrium statistical mechanics*, in particular: **RB-2**, Lifshitz and Pitaevskii, Akhiezer and Peletminskii, Kreuzer, Klimontovich, McLennan, Reichl, Kubo et al.

Chapter 4

Reduced Distribution Functions — and Correlation Functions

4.1 Classification of Dynamical Functions

In dealing specifically with non-equilibrium statistical physics we devise a very useful new formalism. Its main purpose is the elimination from the start of information that is irrelevant for the matters considered here and the elaboration of clear and well-defined approximations. We consider, as usual, a system of N interacting particles, treated in classical mechanics.

In the present and forthcoming chapters we use systematically the compact notation x_j to denote the set of coordinate $\mathbf{q}_j$ and conjugate canonical momentum $\mathbf{p}_j$ of particle j [see Eq. (2.11)]:

$$x_j \equiv (\mathbf{q}_j, \mathbf{p}_j), \quad j = 1, ..., N. \tag{4.1}$$

The Hamiltonian of our system is a function of all variables $(x_1, x_2, ..., x_N)$; it can be written in the following specific form (2.23)-(2.27):

$$H(x_1, x_2, ..., x_N) = \sum_{j=1}^{N} H^0(x_j) + \sum_{j<}^{N} \sum_{k=1}^{N} V(x_j, x_k) \tag{4.2}$$

It was already stressed in Sec. 2.4 that the free-particle Hamiltonian is a *sum of terms* $H_j^0 \equiv H^0(x_j)$, *all of the same functional form, each one depending on a single variable* x_j. The interaction term, on the other hand, is *a sum of terms* $V_{jk} \equiv V(x_j, x_k)$, *all of the same functional form, each one depending non-additively and symmetrically on two variables,* x_j, x_k.

This type of functional dependence is characteristic of the great majority of physically interesting quantities. Thus, the mass density defined and discussed in Sec.

2.3, Eq. (2.21) is a typical example of a dynamical function which is a sum of single variable functions, like H^0; in the present notation, it is written as:

$$\rho(x_1, ..., x_N; \mathbf{x}) = \sum_{j=1}^{N} m\, \delta\left(\mathbf{q}_j - \mathbf{x}\right). \tag{4.3}$$

All other local densities (for instance, the momentum density) are of the same form: the mass m is then replaced in Eq. (4.3) by the appropriate single-particle dynamical function (e.g., the momentum $\mathbf{p}_j$).

We now generalize Eq. (4.3) as follows. Consider an *arbitrary dynamical function of a system of N identical particles*: $b(x_1, ..., x_N)$. As a result of the identity of the particles, this is necessarily a *symmetrical function* under a permutation of any two particles:

$$b(x_1, ..., x_j, ..., x_k, ..., x_N) = b(x_1, ..., x_k, ..., x_j, ..., x_N). \tag{4.4}$$

Any such function can be represented, in a unique way, in the following form:

$$\begin{aligned} b(x_1, ..., x_N) &= b_0 + \sum_{j=1}^{N} b_1(x_j) + \sum_{j<}\sum_{k=1}^{N} b_2(x_j, x_k) \\ &\quad + \sum_{j<}\sum_{k<}\sum_{n=1}^{N} b_3(x_j, x_k, x_n) + ... + b_N(x_1, ..., x_N). \end{aligned} \tag{4.5}$$

Here $b_s(x_1, ..., x_s)$ is a *non-additive* symmetric function of the s variables $x_1, ..., x_s$. (If it were a sum of functions, it would be included in b_k with $k < s$). In order to ensure the symmetric character of the function $b(x_1, ..., x_N)$, the terms $b_1(x_j)$ must represent the *same* function of the different variables x_j, $j = 1, ..., N$; a similar definition holds for $b_2, b_3, ...$ b_0 is a constant. The functions b_s will be called *irreducible s-particle dynamical functions*.

Remark. Let us explain in detail the summation prescription in Eq. (4.5). Clearly, in the term $b_2(x_j, x_k)$ the particles j and k must be different, otherwise this term would be included in a function of type b_1. But if we merely prescribe $j \neq k$, every couple of particles would be counted twice: we therefore require $j < k$. Thus, for instance, for $N = 3$:

$$\sum_{j<}\sum_{k=1}^{N} b_2(x_j, x_k) = b_2(x_1, x_2) + b_2(x_1, x_3) + b_2(x_2, x_3).$$

Alternatively, we may also require that the summations are done with the prescription $j \neq k$: in that case, the overcounting is avoided by dividing the result by s! Eq. (4.5) is then written as:

$$b(x_1, ..., x_N) = b_0 + \sum_{j=1}^{N} b_1(x_j) + \frac{1}{2!} \sum_{j \neq}^{N} \sum_{k=1}^{N} b_2(x_j, x_k)$$

$$+ \frac{1}{s!} \sum_{j \neq}^{N} \sum_{k \neq}^{N} \sum_{n=1}^{N} b_3(x_j, x_k, x_n) + ... + b_N(x_1, ..., x_N). \qquad (4.6)$$

Most often, whenever the context is unambiguous, we write a single explicit summation (or integration) sign in formulae involving multiple summations (or integrations).

It appears that most dynamical functions of interest have only two or three non-zero terms in the expansion (4.5). Consider, for instance, the interaction potential in the Hamiltonian (4.2). We could have a term of the form $V(x_j, x_k, x_n)$. This term would imply that the presence of a third particle n changes the potential energy of the couple j, k in addition to the sum of direct two-body interaction energies (j, n), (k, n). Such a three-body correlation effect is very small, and usually unobservable. From this discussion we conclude that *practically all dynamical functions of real physical interest, when represented in the form (4.5) contain only a finite, generally small number of irreducible dynamical functions: $b_0, b_1, ..., b_S$, with $S \ll N$. For these dynamical functions $b_s = 0$ for $s > S$* (most often $S = 2$ or 3). By representing the dynamical functions in the form (4.5) we uncovered a very simple characteristic feature, which we now exploit in the development of the general formalism of statistical mechanics.

4.2   Reduced Distribution Functions

Consider the observable, average value of a dynamical function $b(x_1, ..., x_N)$ represented in the form (4.6). The statistical state of the system is determined, according to the rules of classical statistical mechanics, by the phase space distribution $F(x_1, ..., x_N; t)$. [In the rest of this section, the argument t will be implicitly understood, but will not be written down]. All the particles being identical, this function is symmetric under the permutation of its arguments:

$$F(x_1, ..., x_j, ..., x_k, ...x_N) = F(x_1, ..., x_k, ..., x_j, ...x_N) \qquad (4.7)$$

We now use the basic formula (3.6) to calculate the average value of a dynamical function of the form (4.6). The term b_0 simply yields the constant b_0 itself [see Eq. (3.3)]. The contribution of the one-particle irreducible functions is:

$$\int dx_1 .. dx_N \left[\sum_{j=1}^{N} b_1(x_j) \right] F(x_1, ..., x_N)$$

$$= N \int dx_1..dx_N \ b_1(x_1) \, F(x_1, ..., x_N) \tag{4.8}$$

Indeed, by symmetry, each term in the sum of the left hand side yields the same integral, hence the sum equals N times the contribution of any one of the summands, e.g., of $j = 1$. We now note that all integrations, except the one over x_1, involve only the function F. We thus introduce a new object, called the *reduced one-particle distribution function* $f_1(x_1)$:

$$f_1(x_1) = N \int dx_2..dx_N \ F(x_1, x_2, ..., x_N) \tag{4.9}$$

In terms of this function, the average of Eq. (4.8) is written in the following very simple form:

$$\int dx_1..dx_N \ \left[\sum_{j=1}^{N} b_1(x_j) \right] F(x_1, .., x_N) = \int dx_1 \, b_1(x_1) \, f_1(x_1).$$

The conclusion is clear: in order to calculate the average of a sum of one-particle dynamical functions b_1 it is not necessary to know the extraordinarily complicated function $F(x_1, .., x_N)$. The knowledge of a much simpler function of a single variable x_1 is sufficient for this operation.

Consider now the general term of Eq. (4.6). Because of the symmetry, the average of the s-fold sum consists of $[N!/(N-s)!s!]$ equal terms ($=$ number of ways of choosing s particles among N]:

$$\int dx_1..dx_N \ \left[\frac{1}{s!} \sum_{j_1 \neq}^{N} .. \sum_{j_s=1}^{N} b_s(x_{j_1}, ..., x_{j_s}) \right] F(x_1, ..., x_N)$$

$$= \frac{N!}{(N-s)!s!} \int dx_1..dx_s..dx_N \ b_s(x_1, ..., x_s) \, F(x_1, ..., x_s, ..., x_N). \tag{4.10}$$

We now define the s-PARTICLE REDUCED DISTRIBUTION FUNCTION $f_s(x_1, ..., x_s)$, $s \leq N$:

$$f_s(x_1, ..., x_s) = \frac{N!}{(N-s)!} \int dx_{s+1}..dx_N \ F(x_1, ..., x_s, x_{s+1}, ..., x_N). \tag{4.11}$$

The physical meaning of this quantity is clear. The s-particle reduced distribution function $f_s(x_1, ..., x_s)$ represents [up to the factor $N!/(N-s)!$] the probability density of finding simultaneously the s particles in the specified positions $x_1, ..., x_s$. It is clearly a symmetric function:

$$f_s(x_1, ..., x_j, ..., x_k, ..., x_s) = f_s(x_1, ..., x_k, ..., x_j, ..., x_s). \tag{4.12}$$

Note the particular case [resulting from the normalization condition (3.7)]:

$$f_0 = 1. \tag{4.13}$$

Note also the normalization condition of the reduced distribution functions:

$$\int dx_1..dx_s \, f_s(x_1, ..., x_s) = \frac{N!}{(N-s)!}. \tag{4.14}$$

The reduced distribution functions are not independent of each other. As they are all deriving from the same phase space distribution function F, the following relation is easily proved:

$$f_r(x_1, ..., x_r) = \frac{(N-s)!}{(N-r)!} \int dx_{r+1}...dx_s \, f_s(x_1, ..., x_s), \quad r < s \le N. \tag{4.15}$$

Note that this relation cannot be inverted: f_r contains less information than f_s when $r < s$, hence f_s cannot be expressed in terms of f_r alone..

Collecting all these results, we find the following basic expression of the observable average of any dynamical quantity in terms of the reduced distribution functions:

$$\langle b \rangle = \sum_{s=0}^{N} \frac{1}{s!} \int dx_1...dx_s \, b_s(x_1, ..., x_s) \, f_s(x_1, ..., x_s). \tag{4.16}$$

(By definition, the term $s = 0$ involves no integration).

The new representation of statistical mechanics in terms of the complete set of reduced distribution functions ($0 \le s \le N$) is strictly equivalent to the initial representation in terms of the phase space distribution function F. It has many advantages that will be progressively discovered. In particular, as the interesting dynamical functions have the property that $b_s(x_1,...,x_s) \equiv 0$ for $s \ge 2$ or 3, we conclude that *the knowledge of two or three reduced distribution functions is sufficient for the calculation of all relevant macroscopic quantities*. It will presently be seen, however, that the simplicity of this feature is rather illusory.

Statistical physics is the science of large systems. It takes advantage of the large values of the number of particles N and of the volume V (compared to molecular dimensions) in order to simplify the calculations. Whenever such a simplification is possible, it will be "maximal" in the limit $N \to \infty$ and $V \to \infty$. This mathematical limit should be well understood from the physical point of view (where there are no infinite systems). It implies the consideration of a sequence of increasingly large systems; if the limit is taken carefully, the local properties in the bulk of these systems will tend toward a constant value, independent of size, and not influenced by the boundaries. In order to realize this independence, any increase in N must be accompanied by an increase in volume V, in such a way that the average particle density

$n = N/V$ in the system remains constant. Whenever this constraint is satisfied, the value of the local quantities may just as well be calculated for a fictitious system, defined by the limit:

$$T - \lim : \ N \to \infty, \ V \to \infty, \quad N/V = n = const. \tag{4.17}$$

This limiting process is called the THERMODYNAMIC LIMIT: it is a most important operation underlying, explicitly or implicitly, most of statistical dynamics. Its role in equilibrium theory is well known.

It is interesting to discuss the behaviour of the reduced distribution functions in the thermodynamic limit. Note first that the concept of thermodynamic limit is strictly irrelevant for the phase space distribution function F. In order to define this limit, one must compare systems with an increasing number of particles (enclosed in a proportionally increasing volume). But the functions $F(x_1, ..., x_N)$ and $F(x_1, ..., x_{N+1})$ depend on a different number of variables, they belong to different function spaces: it is meaningless to compare them (this would amount to "comparing apples to pears!").

Consider now the value of a reduced distribution function for fixed values of the coordinates $(x_1, ..., x_s)$. The probability of finding the particles in this configuration is influenced by all the particles located within the interaction range of the inter-molecular forces of these distinguished particles. These "influencing" particles belong either to the distinguished group $(1, ..., s)$ or to the complementary set; in the latter case their interaction is averaged over the whole phase space. The function f_s thus depends *parametrically* on the number of particles N and on the volume V. We there-fore write the function as $f_s(x_1, ..., x_s; N, V)$ whenever we need to stress explicitly this parametric dependence.

Consider first a system consisting of exactly s particles $(N = s)$: the distribution function $f_s(x_1, ..., x_s) = F(x_1, ..., x_s)$ has a well defined value for a given configuration $(x_1, ..., x_s)$ (see Fig. 4.1). We now add a particle to the system $(N = s + 1)$, increase the volume proportionally, and average over the position of the new particle, keeping the s initial particles in their fixed configuration. For finite (and relatively small) s, the environment of these particles has changed considerably, and this affects the value of f_s. Adding more and more particles and increasing the volume proportionally, the average environment of the distinguished particles changes less and less (adding an additional particle to an average environment of 10000 particles has a negligible effect). Accordingly, the value of f_s will be less and less changed by this addition: f_s tends towards a constant value. Note that we are now comparing successive values of the *same* function of the variables $(x_1, ..., x_s)$, i.e.: $f_s(x_1, ..., x_s; N, V)$, upon variation of the *parameters* N and V. Thus, the thermodynamic limit is a well defined operation for f_s, in contrast to the phase space distribution function F. It is thus reasonable to formulate the following postulate: *For any finite value of s and for every configuration $(x_1, ..., x_s)$, the reduced distribution functions $f_s(x_1, ..., x_s; N, V)$ tend toward a finite*
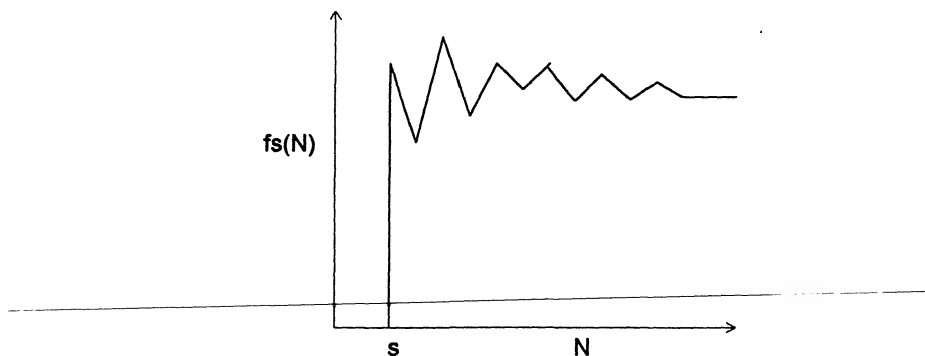
Figure 4.1: Variation of $f_s(x_1, ..., x_s; N)$ with N for a fixed configuration.

limiting value in the thermodynamic limit $N \to \infty$, $V \to \infty$, $N/V = n$; this value is independent of N and V separately (i.e., it depends only on their ratio n).[1] This remarkable property makes it possible, in the treatment of any problem, to go over to the thermodynamic limit at the very beginning: this considerably simplifies the calculations.

We now briefly consider the *normalization* of the reduced distribution functions in the thermodynamic limit. For fixed s and $N \to \infty$, the right hand side of Eq. (4.14) reduces to:

$$N(N-1)...(N-s-1) \to N^s ,$$

hence, Eq. (4.14) can be rewritten as follows:

$$N^{-s} \int dx_1...dx_s \, f_s(x_1, ..., x_s) = 1, \qquad \forall s, \quad (T-\lim) \qquad (4.18)$$

Before closing this section, we discuss the special form taken by the reduced distribution functions in the case of a *spatially homogeneous system* (such systems will be often discussed hereafter, because of their simplicity). In such systems the local (intensive) physical properties are the same at all points in space. This property is expressed mathematically by the *translational invariance* of the reduced distribution functions:

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[1]Note that the existence of the reduced distribution functions in the thermodynamic limit can be proved in full mathematical rigour under very weak assumptions.

$$f_s(\mathbf{q}_1 + \mathbf{a}, ..., \mathbf{q}_s + \mathbf{a}, \mathbf{p}_1, ..., \mathbf{p}_s) = f_s(\mathbf{q}_1, ..., \mathbf{q}_s, \mathbf{p}_1, ..., \mathbf{p}_s) \qquad (4.19)$$

where $\mathbf{a}$ is any constant vector.[2] Strictly speaking, homogeneous systems can only be defined in an infinite volume (hence in the thermodynamic limit). For finite systems, this concept is still quite useful for describing intensive properties in the bulk of the system, far from its boundaries. Because of the constraint (4.19), the reduced s-particle distribution functions effectively depend only on $s - 1$ position variables. In particular, f_1 depends only on the momentum $\mathbf{p}$, and f_2 depends only on the relative distance $\mathbf{q}_1 - \mathbf{q}_2$:

$$f_1(\mathbf{q}, \mathbf{p}) = n\, \varphi(\mathbf{p}) , \qquad (4.20)$$

$$f_2(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) = f_2(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) . \qquad (4.21)$$

where $n = N/V$ is the number density (which is constant for a homogeneous system). For consistency with the normalization condition (4.14) we must have:

$$\int d\mathbf{p}\, \varphi(\mathbf{p}) = 1 . \qquad (4.22)$$

The function $\varphi(\mathbf{p})$ is called the *momentum distribution function.*

4.3   Evolution of the Reduced Distribution Functions

Consider again a classical system of N interacting particles, contained in a finite volume V. We assume the Hamiltonian to be of the form (4.2). The evolution of the system is described exactly by the Liouville equation (3.16), which we rewrite as follows, using Eqs. (3.21) - (3.23):

$$\partial_t F = \sum_{j=1}^{N} L_j^0 F + \sum_{j<}^{N} \sum_{n=1}^{N} L_{jn}' F. \qquad (4.23)$$

From this basic equation we generate a set of equations for the reduced distribution functions. We first prove two elementary lemmas which will be extensively

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[2]Note that the expression (4.19) for the translational invariance condition is only valid for a system of particles, described by canonical variables such that $\mathbf{q}_i$ represents the spatial cartesian coordinates of particle i. For any other choice of phase space variables, or for other types of dynamical systems, the homogeneity condition will be expressed in a different form.

used in forthcoming work. Remember that the conservation of particles requires the normalization condition:

$$\int dx_1...dx_N \ F(x_1,...,x_N;t) = 1, \quad \forall t,$$

from which we conclude:

$$\partial_t \int dx_1...dx_N \ F(x_1,...,x_N;t) = 0, \quad \forall t.$$

thus, from (4.23):

$$\int dx_1...dx_N \ \left\{ \sum_{j=1}^{N} L_j^0 + \sum_{j<}^{N} \sum_{n=1}^{N} L_{jn}' \right\} F = 0.$$

These relations must be valid whatever the number of particles; as a result, each term must vanish separately:

$$\int dx_1...dx_N \ L_j^0 \ F(x_1,...,x_N;t), \quad \forall j, \ \forall t \qquad (4.24)$$

$$\int dx_1...dx_N \ L_{jn}' \ F(x_1,...,x_N;t), \quad \forall j,n, \ \forall t \qquad (4.25)$$

These relations can also be verified directly by using the explicit form of the Liouvillians (3.22), (3.23). Each term involves a derivative of F, either with respect to q or with respect to p. We will always suppose that F together with a sufficient number of derivatives vanishes at the boundaries of the system (or is contained in a parallelipiped with periodic boundary conditions) and that F together with a sufficient number of derivatives vanishes as $p \rightarrow \pm\infty$. Hence, by integration by parts we find:

$$\int d\mathbf{q}_j \frac{\partial}{\partial \mathbf{q}_j} F = 0, \quad \int d\mathbf{p}_j \frac{\partial}{\partial \mathbf{p}_j} F = 0, \qquad (4.26)$$

which imply Eqs. (4.24), (4.25).

We come back to Eq. (4.23). In order to derive an evolution equation for the s-particle reduced distribution function, we use definition (4.11), integrating (4.23) over the particles $s+1,..,N$ and multiplying by the appropriate normalization factor [we do not write explicitly the variable t]:

$$\partial_t f_s(x_1,...,x_s) = \partial_t \frac{N!}{(N-s)!} \int dx_{s+1}...dx_N \ F(x_1,...,x_s,x_{s+1},...,x_N)$$

$$= \frac{N!}{(N-s)!} \int dx_{s+1}..dx_N \ \left\{ \sum_{j=1}^{N} L_j^0 F + \sum_{j<}^{N} \sum_{n=1}^{N} L_{jn}' F \right\}. \quad (4.27)$$

Consider the first bracketted term. We may write:

$$\sum_{j=1}^{N} L_j^0 = \sum_{j=1}^{s} L_j^0 + \sum_{j=s+1}^{N} L_j^0.$$

If j belongs to the group $(1, ..., s)$, L_j^0 is not affected by the integrations, and can therefore be taken in front of the integration sign; if j belongs to the group $(s + 1, ..., N)$, it follows from the lemma (4.24) that the corresponding integrals are identically zero. Hence, using Eq. (4.11), the first term in the right hand side of (4.27) reduces to:

$$\sum_{j=1}^{N} L_j^0 \frac{N!}{(N - s)!} \int dx_{s+1}...dx_N \ F = \sum_{j=1}^{s} L_j^0 f_s(x_1, ..., x_s)$$

The second term in (4.27) is somewhat more complicated. We distinguish three cases.

a. Particles j and n both belong to the group $(1,...,s)$. The operator L'_{jn} can be taken in front of the integrals and we obtain, as above:

$$\sum_{j<}\sum_{n=1}^{s} L'_{jn} \ f_s(x_1, ..., x_s)$$

b. Particles j and n both belong to the group $(s+1,...,N)$. The corresponding contributions are then zero, because of (4.25).

c. Particle j belongs to the group $(1,...,s)$ and particles n $(>j)$ belongs to the group $(s+1,...,N)$. x_n is now a dummy integration variable; because of the symmetry of the function F we may write:

$$\frac{N!}{(N - s)!} \int dx_{s+1}...dx_N \sum_{j=1}^{s} \sum_{n=s+1}^{N} L'_{jn} F(x_1, ..., x_N)$$

$$= \frac{N!}{(N - s)!} \int dx_{s+1}...dx_N \sum_{j=1}^{s}(N - s) L'_{j,s+1} F(x_1, ..., x_N)$$

$$= \frac{N!}{(N - s - 1)!} \int dx_{s+1}dx_{s+2}...dx_N \sum_{j=1}^{s} L'_{j,s+1} F(x_1, ..., x_N)$$

$$= \sum_{j=1}^{s} \int dx_{s+1} L'_{j,s+1} \frac{N!}{(N - s - 1)!} \int dx_{s+2}...dx_N \ F(x_1, ..., x_N)$$

$$= \sum_{j=1}^{s} \int dx_{s+1} L'_{j,s+1} \ f_{s+1}(x_1, ..., x_{s+1}).$$

Collecting all these partial results we obtain the final equations, expressed solely in terms of reduced distribution functions:

$$\partial_t f_1(x_1) = L_1^0 f_1(x_1) + \int dx_2 \, L_{12}' f_2(x_1, x_2) \, , \tag{4.28}$$

$$\partial_t f_s(x_1, ..., x_s) = \sum_{j=1}^{s} L_j^0 f_s(x_1, ..., x_s) + \sum_{j<}^{s} \sum_{n=1}^{s} L_{jn}' \, f_s(x_1, ..., x_s)$$
$$+ \sum_{j=1}^{s} \int dx_{s+1} \, L_{j,s+1}' f_{s+1}(x_1, ..., x_{s+1}) \, , \quad s \ \geq \ 2, \tag{4.29}$$

$$\partial_t f_0 = 0. \tag{4.30}$$

[Note: for $s = 1$ the second term in the right hand side of (4.29) is identically zero (the particle cannot interact with itself. The zeroth order function: $f_0 \equiv 1$: the trivial equation (4.30) will no longer be considered.].

Eqs. (4.28), (4.29) form a *set of N equations for the reduced distribution functions*. They are called the *BBGKY HIERARCHY*; the initials are those of the (numerous) authors who derived it independently: *Bogoliubov - Born - Green - Kirkwood - Yvon* (note that the alphabetical order is not the chronological one: the first author is actually Yvon, who derived it in 1932, whereas the others rederived it independently in the mid-forties).

The most remarkable property of the set (4.29) is its *hierarchical structure*: the determination of the *s*-particle distribution function requires the knowledge of the *higher order* $(s+1)$ particle function. In the thermodynamic limit, we are faced with the problem of solving an infinite set of coupled integro-differential equations: an impossible task. Here we pay the price of the passage from the phase space distribution function F to the reduced distribution functions f_s. Although the knowledge of the first two or three reduced distributions is sufficient for the calculation of all relevant observable quantities, these functions cannot be determined by solving a closed set of two or three equations. Notwithstanding this inescapable difficulty, it will be seen that the reduced distribution functions formalism has very great advantages, which makes it a precious tool for the study of non-equilibrium phenomena.

Before closing this section, we introduce a *graphical representation* of Eqs. (4.28), (4.29) that will prove very useful in the forthcoming developments. An *s*-particle distribution function $f_s(x_1, ..., x_s)$ will be represented by a set of *s* superposed horizontal dotted lines labeled $(1, ..., s)$. The free propagation operator L^0 will not require any special symbolic representation. The interactions, on the other hand, seriously affect the state of the system by introducing correlations between the partners. We represent an interaction operator L_{jn}' by a vertex joining the lines j and n coming in from the right. There are two types of terms involving this operator. One is diagonal in the number of particles (interactions within the group of particles considered): this

will naturally be expressed by the same two particle lines coming out to the left. This type of diagram will be called an *X-vertex*. The other type involves the interaction with an extra particle, followed by an integration over the coordinates of the latter. It represents a transition from an $(s+1)$-particle state to an s-particle state: a single line comes out of the vertex to the left. This type of diagram will be called an *Y-vertex*. The diagrams representing the first two equations of the BBGKY hierarchy are shown in Figs. 4.2 and 4.3, which are self-explanatory. (The reason for using dotted lines will appear in Sec. 4.5).
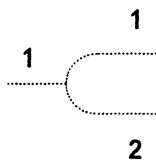
Figure 4.2: Diagram for the evolution of the RDF $f_1(1)$.
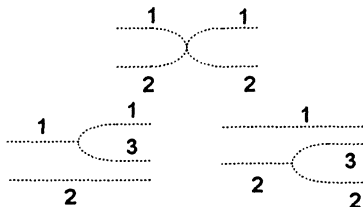
Figure 4.3: Diagrams for the evolution of the RDF $f_2(1,2)$.

For certain forthcoming applications, it is convenient to use the Fourier transform of the reduced distribution functions with respect to the position variables $(\mathbf{q}_1, ..., \mathbf{q}_s)$:

$$f_s(\mathbf{q}_1, \mathbf{p}_1, ..., \mathbf{q}_s, \mathbf{p}_s; t) = \int d\mathbf{k}_1 ... d\mathbf{k}_s \, \exp\left(\sum_{j=1}^{s} i\mathbf{k}_j \cdot \mathbf{q}_j\right) \tilde{f}_s(\mathbf{k}_1, \mathbf{p}_1, ..., \mathbf{k}_s, \mathbf{p}_s; t).$$

$$(4.31)$$

This formula is inverted as follows:

$$\tilde{f}_s(\mathbf{k}_1, \mathbf{p}_1, ..., \mathbf{k}_s, \mathbf{p}_s; t) = (2\pi)^{-3} \int d\mathbf{q}_1 ... d\mathbf{q}_s \, \exp\left(-\sum_{j=1}^{s} i\mathbf{k}_j \cdot \mathbf{q}_j\right) f_s(\mathbf{q}_1, \mathbf{p}_1, ..., \mathbf{q}_s, \mathbf{p}_s; t)$$
$$(4.32)$$

We shall often use the abbreviation $\tilde{f}_s(\xi_1, ..., \xi_s; t) = \tilde{f}_s(\mathbf{k}_1, \mathbf{p}_1, ..., \mathbf{k}_s, \mathbf{p}_s; t)$. The Liouvillians in the Fourier representation are easily determined from Eqs. (3.22), (3.23):

$$L_1^0 \tilde{f}_1(\xi_1) = -i\mathbf{k}_1 \cdot \mathbf{v}_1 \tilde{f}_1(\mathbf{k}_1, \mathbf{p}_1), \qquad\qquad (4.33)$$

$$L_{12}' \tilde{f}_2(\xi_1, \xi_2) = \int d\mathbf{l} \, \tilde{V}(\mathbf{l}) \, i\mathbf{l} \cdot \partial_{12} \, \tilde{f}_2(\mathbf{k}_1 - \mathbf{l}, \mathbf{p}_1, \mathbf{k}_2 + \mathbf{l}, \mathbf{p}_2), \qquad (4.34)$$

where $\tilde{V}(\mathbf{l})$ is the Fourier transform of the interaction potential, (2.31).

4.4   Correlation Functions

The reduced distribution functions of more than one particle introduce the basic concept of *correlations*. Consider a s-particle distribution function at a fixed time. It may happen that this function is in the form of a product of one-particle distribution functions:

$$f_s^{unc}(x_1, ..., x_s; t) = \prod_{j=1}^{s} f_1(x_j; t).$$
$$(4.35)$$

In this case, the system is said to be in an *uncorrelated state*. In such a state, the particles are statistically independent from each other; that is, the probability of finding a particle at some point is not influenced by the presence of any other particle at any other point.

In general, however, Eq. (4.35) is not true, in particular, because of the existence of mechanical *interactions* among the particles. As a result, every particle influences the behaviour of its neighbouring particles, hence creating correlations. The importance of this effect clearly depends on the distance between the particles, and tends to zero when this distance becomes very large: correlations thus possess a (usually) finite *range*. The correlation range is at least equal to the range of the intermolecular forces. Even though, in many usual situations, their ranges are of the same order, the correlation range may become quite large as a result of cooperative interactions involving a chain of successive nearest neighbours. In particular, the correlation range becomes very large and even tends to infinity near the critical point of a phase transition (although the range of the interactions is finite). This point will be further treated in

Chap. 13. It shows that a clear distinction should be made between interactions and correlations. Indeed, interactions always produce correlations, but correlations can also be produced by other means, such as an appropriate external preparation of the system. A specially important cause of correlations that is completely independent of dynamical interactions is the effect of quantum statistics: this effect will not be examined in the present book, devoted to classical mechanics [see **RB-2**, or other references in **BN3**].

The presence of correlations can always be described by using the following representation of the distribution functions:

$$f_s(x_1, ..., x_s) = \prod_{j=1}^{s} f_1(x_j) + g_s'(x_1, ..., x_s) \ . \tag{4.36}$$

The function $g_s'(x_1, ..., x_s)$ represents pretty trivially the deviation of the true distribution function from its uncorrelated form. In many cases, this representation does not yield sufficient information. For $s = 2$, $g_2'(x_1, x_2)$ cannot be further analyzed. For $s = 3$, however, we can imagine situations in which particles 1 and 2 are correlated, the third one being independent (e.g., because it is far away), or particles $1, 2, 3$ are mutually correlated. In neither case is the three-particle function a product of three one-particle functions, but the type of correlation is different in the two cases. In order to analyze all situations, we consider all possible *partitions of the set (1,...,s) into disjoint subsets containing at least one particle.* Interpreting each subset, or *cluster*, as representing a group of mutually correlated particles, statistically independent of the other subsets, we obtain the following *cluster representation* of the reduced distribution functions for $s \geq 2$:

$$f_2(x_1, x_2) = f_1(x_1)f_1(x_2) + g_2(x_1, x_2) \ , \tag{4.37}$$

$$
\begin{aligned}
f_3(x_1, x_2, x_3) = \ & f_1(x_1)f_1(x_2)f_1(x_3) + f_1(x_1)g_2(x_2, x_3) \\
& + f_1(x_2)g_2(x_1, x_3) + f_1(x_3)g_2(x_1, x_2) \\
& + g_3(x_1, x_2, x_3) \ ,
\end{aligned} \tag{4.38}
$$

and so on. The (irreducible) *correlation functions* $g_s(x_{i_1}, ..., x_{i_s})$ are defined by these successive equations. They are symmetric functions under permutations of the particle labels:

$$g_s(..., x_j, ..., x_n, ...) = g_s(..., x_n, ..., x_j, ...) \ . \tag{4.39}$$

Each (additive) term in the right hand side of Eqs. (4.37), (4.38) is called a *correlation pattern*. We could now devise compact systems of notation in order to abbreviate

formulae like (4.38) for arbitrary numbers of particles and for arbitrary types of correlation patterns. For the problems discussed in the present book, however, we shall not need such a degree of generality [see **RB-2**].

We now derive the normalization properties of the correlation functions. Consider Eq. (4.37), divide both sides by N^2, and integrate over the variables x_1, x_2:

$$N^{-2} \int dx_1 dx_2 \, f_2(x_1, x_2) \; = \; \left\{ N^{-1} \int dx_1 \, f_1(x_1) \right\} \left\{ N^{-1} \int dx_2 \, f_1(x_2) \right\}$$
$$+ N^{-2} \int dx_1 dx_2 \, g_2(x_1, x_2) \, .$$

In the *thermodynamic limit*, the left hand side equals 1 because of Eq. (4.18); by the same equation, the first term in the right hand side also equals 1, hence the second term must vanish. This result is generalized as follows:

$$N^{-s} \int dx_1 ... dx_s \, g_s(x_1, ..., x_s) = 0, \quad s \geq 2 \quad (T - \lim) \tag{4.40}$$

It then follows that, in the thermodynamic limit, the whole normalization of $f_s(x_1, ..., x_s)$ is contained in the uncorrelated term of the cluster representation (4.37), (4.38): all other correlation patterns contribute zero to the normalization integral.

An important conclusion of this section is that the statistical state of the system is completely described by the set consisting of the one-particle reduced distribution function f_1 and the set of all correlation functions g_s as shown by Eqs. (4.37), (4.38). In order to simplify the terminology, we henceforth delete the subscript "1" on the former, and call $f(x_1; t)$ "the" reduced distribution function, abbreviated as (RDF). The set $\{f, g_s\}$, $s \geq 2$, will be called the *correlation representation* of the statistical state of the system.

4.5 Evolution of the Correlation Functions

A set of equations of evolution for the correlation functions $g_s(x_1, ..., x_s)$ is easily obtained from the BBGKY equations (4.28), (4.29), by substituting the cluster representation (4.37), (4.38), etc. The calculations become, however, tedious for the higher order correlations. A graphical method will help us in providing insight in the numerous terms appearing in these equations. The method is a refinement of the diagrams introduced in Sec. 4.3 (Figs. 4.2, 4.3).

We represent again the state of the system by a set of superposed lines, but add an additional element of information in order to describe the particular pattern of correlation. We represent *correlated particles* by a set of *connected lines*. In absence of further information about the origin of the correlation, the connection is materialized by an arc connecting the horizontal lines at the right hand side of the diagram.

The new diagrams will be drawn with solid lines. The unperturbed Liouvillian will not be represented by any special symbol because in the BBGKY equations it always connects correlation patterns of the same type. The interaction Liouvillians are represented by the vertices introduced in Figs. 4.2 and 4.3, but now the resulting figures should be analyzed in order to determine the correlation pattern produced by the interaction. We illustrate the procedure by the first two equations.

- $s=1$.

Substituting Eq. (4.37) into (4.28) we obtain:

$$\partial_t f(x_1) - L_1^0 f(x_1) = \int dx_2 \left[L_{12}' f(x_1)f(x_2) + L_{12}' g_2(x_1, x_2) \right] . \qquad (4.41)$$

(Here and below, the time argument is not written down explicitly). The right hand side of this equation is represented by the diagrams of Fig. 4.4.
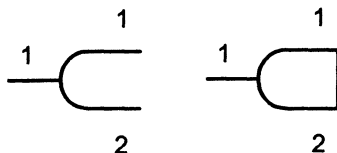
Figure 4.4: Diagrams for the evolution of the RDF $f(1)$.

- $s=2$.

Substituting now Eqs. (4.37), (4.38) into the second equation of the BBGKY hierarchy, (4.29), we obtain:

$$\partial_t f_2(x_1, x_2) - \left[L_1^0 + L_2^0 \right] f_2(x_1, x_2) = L_{12}' \left[f_1(x_1)f_1(x_2) + g_2(x_1, x_2) \right]$$
$$+ \int dx_3 \left\{ L_{13}' \left[f_1(x_1)f_1(x_2)f_1(x_3) + f_1(x_1)g_2(x_2, x_3) + f_1(x_2)g_2(x_1, x_3) \right. \right.$$
$$\left. \left. + f_1(x_3)g_2(x_1, x_2) + g_3(x_1, x_2, x_3) \right] + (1 \leftrightarrow 2) \right\} . \qquad (4.42)$$

We introduce provisionally the notation: $D_{1...j} \equiv \partial_t - \left[L_1^0 + \cdots + L_j^0 \right]$ and note that the left hand side of Eq. (4.42) can be written as:

$$D_{12}f_2(x_1, x_2) = f_1(x_1) D_2 f_1(x_2) + f_1(x_2) D_1 f_1(x_1) + D_{12}g_2(x_1, x_2)$$

$$(4.43)$$

Our strategy consists of identifying among the many terms of Eq. (4.42) those which contribute to each of the three terms of Eq. (4.43). Recalling that the expressions $D_j f_1(x_j)$ were determined in (4.41), this exercise is easy, but becomes rather tedious in higher orders. The diagram technique will help us in achieving this purpose. The practical rule, which is easily understood, is the following.

- 1. ~~Draw all the diagrams contributing to $D_{1...s}f_s(x_1, ..., x_s)$~~ as in Fig. 4.3.

- 2. Replace each diagram by a sum of diagrams corresponding to all possible patterns describing the "initial" state (on the right).

- 3. Among all diagrams, pick out those that are completely connected: these are the contributions defining $D_{1...s}g_s(x_1, ..., x_s)$. [The remaining, partially or totally disconnected diagrams contribute to the other correlation patterns appearing in $f_s(x_1, ..., x_s)$].
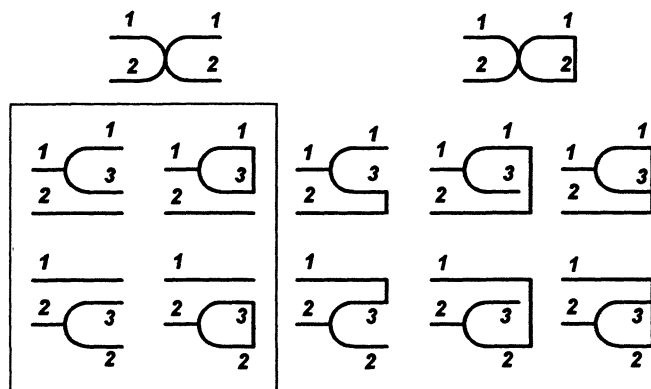
Figure 4.5: Diagrams for the evolution of the correlation function $g_2(1, 2)$. [The framed diagrams contribute to the evolution of $f(1)$ $f(2)$].

The illustration of the procedure is given in Fig. 4.5. Discarding the disconnected diagrams that are shown within the frame, and translating the diagrams into mathematical expressions, we find (setting $f_1 \to f$):

$$\partial_t g_2(x_1, x_2) - \left[L_1^0 + L_2^0\right] g_2(x_1, x_2) = L_{12}' f(x_1) f(x_2) + L_{12}' g_2(x_1, x_2)$$
$$+ \int dx_3 \left\{ L_{13}' f(x_1) g_2(x_2, x_3) + L_{23}' f(x_2) g_2(x_1, x_3) \right.$$
$$\left. + (L_{13}' + L_{23}') \left[f(x_3) g_2(x_1, x_2) + g_3(x_1, x_2, x_3)\right] \right\} . \qquad (4.44)$$

Eqs. (4.41), (4.44) will be the starting point for our forthcoming derivation of classical kinetic equations.

An important, though obvious remark can be made at this point: *the equations for the correlation functions g_s are necessarily* NONLINEAR, contrary to the original BBGKY equations for the distribution functions f_s, which are linear. The origin of this feature is, clearly, the nonlinear relationship between f_s and g_s [see Eqs. (4.37), (4.38)]. This complication is unavoidable; on the other hand the representation in terms of correlation functions is the only way of analyzing the evolution process physically and defining clear approximation schemes, as will be seen in forthcoming chapters.

4.6   Bibliographical Notes BN4

The reduced distribution functions were introduced by the following authors, who discovered the hierarchy independently. The name of this hierarchy remains one of the great injustices of history: Yvon had published the result 14 years before the others, but his work went unnoticed!

Yvon, J., 1935, *La théorie statistique des fluides et l'équation d'état,* Actualités scientifiques et industrielles, No. 203, Hermann, Paris,
Bogolioubov, N.N., 1946, J. Phys. USSR, **10**, 257, 265,
Born, M. and Green, H.S., 1946, Proc. Roy. Soc., London, **A188**, 10,
Kirkwood, J.G., 1946, J. Chem. Phys., **14**, 180.

General discussions of these functions can be found in the following books:

Green, H.S., 1952, *The molecular theory of fluids,* North Holland, Amsterdam,
Massignon, D., 1957, *Mécanique statistique des fluides,* Dunod, Paris,
Yvon, J., 1965, *Les corrélations et l'entropie,* Dunod, Paris,
Münster, A., 1969, (see **BN3**),
Balescu, R., 1975 (**RB-2**, see **BN3**).

A mathematical discussion of the BBGKY hierarchy is given in:

Galavotti, G., Lanford, O.E. and Lebowitz, 1970, J. Math. Phys., **11**, 2898.

The *correlation patterns* as defined here were introduced and used extensively by:

Balescu, R., 1971, Physica, **54**, 1 (see also **RB-2**).

The BBGKY hierarchy was transformed into a nonlinear set of equations for the correlation functions by several authors; we mention here:

Green, M.S., 1956, J. Chem. Phys., **25**, 836,
Cohen, E.G.D., 1956, Physica, **28**, 1025.

The extensive exploitation of the idea of *dynamics of correlations* is due to Prigogine, who used a somewhat different definition of the correlations (Fourier components of the N-body distribution function):

Prigogine, I., 1963, (see **BN3**); see also:
Balescu, R., 1963, (**RB-1**, see **BN1**).

Chapter 5

The Mean Field Approximation

5.1 Weakly Coupled Systems

From here on we consider applications of the general formalism developed in previous chapters. We were faced at the end of Chap. 4 with a rather formidable programme expressed as an infinite hierarchy of equations for the correlation functions. It turns out, however, that for several important classes of systems this hierarchy can be very significantly simplified. Essentially, for such systems the correlation functions of order higher than a certain number S (i.e., g_s for $s > S$) can be neglected, whereas correlation functions of lower order (i.e., g_s for $s \leq S$) can be expressed as functionals of the one-particle reduced distribution function. As a result, the evolution of these systems is described by a *closed equation for the one-particle reduced distribution function (RDF)* $f(x_1; t)$. Whenever the conditions for this reduction of the description is realized we say that the system is in a *kinetic regime*, and the final equation of evolution for $f(x_1; t)$ is called a KINETIC EQUATION.[1] As will be seen in forthcoming chapters, there exist many different kinetic equations. Their specific form is determined by the nature of the system (gas, solid, liquid, plasma,...), the nature of the intermolecular interactions (shape of the potential, intensity and range of the interactions,...) and the value of the parameters fixing the macroscopic state of the system (density, temperature,...). According to the philosophy of the present book, we do not intend to dwell in detail on the general formal theory of the kinetic equations, but rather consider a number of important special cases, treated as simply as possible. Four important kinetic equations will be derived in Chaps. 5 - 8, relating to widely different types of systems. A discussion of their general properties is given in Chap. 9: it appears that these equations have a number of important common

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[1]The name "kinetic equation" is used here in a rather loose way as a closed equation for the RDF. In Chap. 7 this concept will be restricted to a more precise class of evolution equations (see also the conclusions of the present chapter).

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properties, in spite of the different nature of the systems they describe. Their use for the calculation of macroscopic non-equilibrium quantities is illustrated in Chap. 10.

Before starting the calculations, we note that in classical kinetic theory the *velocity* **v** is a more convenient phase space variable than the momentum **p**. We therefore switch over to this variable in forthcoming chapters. The change of variables $\mathbf{p} = m\mathbf{v}$ is trivial: one should simply insert factors m in appropriate places. Thus, the RDF's are related as follows:

$$f(\mathbf{q}, \mathbf{p}; t) = m^3 f(\mathbf{q}, m\mathbf{v}; t) \equiv m^3 \widehat{f}(\mathbf{q}, \mathbf{v}; t).$$

This relation ensures the validity of the normalization condition in the form:

$$\int d\mathbf{q}\, d\mathbf{p}\, f(\mathbf{q}, \mathbf{p}; t) = \int d\mathbf{q}\, d\mathbf{v}\, \widehat{f}(\mathbf{q}, \mathbf{v}; t) = N.$$

For simplicity, we always suppress the hat on $\widehat{f}(\mathbf{q}, \mathbf{v}; t)$. In this new context, we redefine: $x_j = (\mathbf{q}_j, \mathbf{v}_j)$; moreover, the following symbols are redefined: $\partial_j = \partial/\partial\mathbf{v}_j$, $\partial_{jn} = \partial_j - \partial_n$.

Practically all kinetic equations of real interest in practice are derived by using some form of *perturbation theoryi.* But, as will soon be apparent, one must be very careful in handling this mathematical tool in order to obtain meaningful results. The general strategy of perturbation theory for the solution of an equation of evolution is well known. One starts from an exactly known reference solution (which may possibly be physically trivial). Next, one considers a state that is very close to the reference state: the "distance" between the two is measured by a *small parameter*. The various quantities of interest are then expanded in power series of the small parameter. The choice of a physically relevant small parameter in a given problem is the essential step in the application of these methods to kinetic theory. The leading order in such an expansion should describe as well as possible the class of systems considered. The next terms in the peturbation expansion yield complicated equations, producing only small corrections that are usually not worth the effort of solving these equations.

The most "natural" first choice of a small parameter from a purely mathematical point of view is suggested by the structure of the evolution equations (4.41), (4.44). The *reference state* is defined as one in which all interactions are "switched off": the resulting equations are easily solved exactly (Sec. 5.2). Next, it is assumed that *the strength of the interaction potential $V(r)$ is uniformly small for all distances.* This condition can be formalized as follows. We introduce a dimensionless parameter λ and write (without loss of generality):

$$V(r) \equiv \lambda\, v(r). \tag{5.1}$$

A WEAKLY COUPLED SYSTEM is defined by the following conditions:

$$\lambda \ll 1, \qquad \left| \frac{v(r)}{v(r_0)} \right| = O(1), \quad \forall r, \qquad (5.2)$$

where r_0 is an arbitrary finite length. The conditions expressed by these two equations can also be written more compactly as:

$$|V(r)| = O(\lambda). \qquad (5.3)$$

This equation must be supplemented by the obvious condition that the unperturbed Hamiltonian (i.e., the kinetic energy) is, on the average, a quantity of zeroth order:

$$\left| H^0(v) \right| = O(\lambda^0). \qquad (5.4)$$

Weakly coupled systems lead to the simplest possible non-trivial kinetic equation possessing all essential features of the generic equations of this kind. For this reason, this equation will be treated as a "paradigm" of a kinetic equation in this book. It could rightly be objected, however, that no real intermolecular interaction potential satisfies the conditions (5.2). Indeed, all molecules possess a "hard core"; hence the intermolecular forces become infinitely repulsive as $r \to 0$: the weak coupling condition breaks down at short distances [see the discussion in Sec. 2.4]. The solution to this difficulty will be given in Chap. 7. There exists, however, a class of systems for which the weak coupling condition is a reasonable approximation. This is the case for weak *long range interactions*, the most important example being the fully ionized PLASMAS, whose charged particles interact through Coulomb forces. Because of their slow decay, these forces act on particles at relatively large distance [where (5.3) is satisfied] and very close, violent encounters are very rare. As a result, the kinetic theory of weakly coupled systems is quite currently (and quite successfully) applied to the description of plasmas.[2]

Eqs. (5.3), (5.4) produce a number of consequences. The following one, concerning the ordering of the Liouvillians, is trivial:

$$L_j^0 = O(\lambda^0), \quad L'_{jn} = O(\lambda). \qquad (5.5)$$

The next, very important assumption, concerns the ordering of the correlation functions. As follows from the discussion of Sec. 4.4, the distribution function (RDF) is normalized to one (4.18), and carries the complete normalization of the statistical state (even when $\lambda = 0$); hence necessarily the leading order of this function is:

$$f(x_1; t) = O(\lambda^0). \qquad (5.6)$$

---

[2]It will be seen below that the long range of the interactions introduces another kind of difficulties, which will be treated in Chap. 8.

On the other hand, at least one interaction process (an X-vertex) is needed for producing a 2-particle correlation $g_2(1, 2)$ out of an uncorrelated state; at least two such processes (e.g.: $1 - 2$, $1 - 3$) are required for building up a three-body correlation $g_3(1, 2, 3)$, etc. Hence we may assume the following ordering for the correlations:

$$g_2(x_1, x_2; t) = O(\lambda), \quad g_3(x_1, x_2, x_3; t) = O(\lambda^2), ... \quad (5.7)$$

The following point should be clear. Eqs. (5.6), (5.7) are statements about the leading order of magnitude of the correlations *at all times*; this is, in principle a logically illicit procedure. The assumptions (5.6), (5.7) should refer to the order of magnitude of the functions at a *fixed time, say $t = 0$*; the values at later times cannot be prescribed, but are determined by the equations of evolution. It will, however, easily be checked that the latter maintain these orders of magnitude for all times: the ordering (5.6), (5.7) is *self-consistent*.

Having specified the strength of the interactions and of the correlations, we must say something about their *range*. We know from Eq. (2.27) that the interaction potential depends only on the absolute value of the relative distance $\mathbf{r}_{21} \equiv \mathbf{q}_2 - \mathbf{q}_1$ of the particles: $V(\mathbf{q}_1, \mathbf{q}_2) = V(r_{12})$. The correlation functions can always be represented as functions of the position of one particle (say, $\mathbf{q}_1$) and the relative distances: $g_2(x_1, x_2; t) = g_2(\mathbf{q}_1, \mathbf{r}_{21}, \mathbf{v}_1, \mathbf{v}_2; t)$, $g_3(x_1, x_2, x_3; t) = g_3(\mathbf{q}_1, \mathbf{r}_{21}, \mathbf{r}_{31}, \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3; t)$, etc. We assume that the interaction potential has a *finite range, l_0* [see Sec. 2.4]. This means that the function $V(r)$ depends on a characteristic parameter, having the dimension of length[3], such that:

$$V(r) \approx 0 \quad for \, r \gg l_0. \quad (5.8)$$

Similarly, the correlation functions have finite ranges $l_{C2}, l_{C3}, ...$ which are usually (but not always!) of the same order as l_0 (because the interactions are the main source of the correlations). Excluding here situations such as the neighbourhood of a critical point, where the correlation lengths become very large, we assume that all these quantities are of the same order and define a unique *correlation length l_C* as:

$$l_C = Max\,(l_0, \, l_{C2}, \, l_{C3}, ...) \quad (5.9)$$

We thus deduce the following property:

$$g_2(\mathbf{q}_1, \mathbf{r}_{21}, \mathbf{v}_1, \mathbf{v}_2; t) \approx 0 \quad for \, r_{21} \gg l_C. \quad (5.10)$$

The parameter l_C appears to be an important "yardstick" in kinetic theory.

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[3]The problem of the "range" of the Coulomb potential was mentioned in Sec. 2.4. It will be considered again more rigourously in Chap. 8.

5.2   Free Particle Dynamics

We now consider the law of evolution of a classical system of *non-interacting particles*, i.e., we set $\lambda = 0$, hence $L'_{jn} = 0$. As explained above, this system will be taken as the reference system in the sense of perturbation theory. It is called an *ideal system:* it is well known and extensively discussed in all books on equilibrium statistical mechanics (e.g., **RB-2**). In the latter case it has well defined thermodynamic properties that appear as limiting values when the density $n \to 0$ and/or the temperature $T \to \infty$. On the other hand, ideal systems have no interesting non-equilibrium properties: it will be seen that the transport cefficients become infinite in the limit $\lambda \to 0$. The only use of these systems is to provide a starting point for perturbation theory.

For $\lambda = 0$, the equations for the RDF and for the correlation functions (4.41), (4.44) reduce to:

$$\begin{aligned} \partial_t f(x_1; t) &= L_1^0 f(x_1; t) \\ \partial_t g_2(x_1, x_2; t) &= \left(L_1^0 + L_2^0\right) g_2(x_1, x_2; t), \; etc. \end{aligned} \tag{5.11}$$

We note that the distribution function $f(x_1; t)$ obeys a closed equation: the objective of the kinetic theory is thus realized, albeit trivially, in this system. Next, we note that the RDF and all correlation functions obey *decoupled equations*. As a result, the free particle dynamics cannot create or destroy any correlations.

The equation for the RDF is very easily solved. We introduce an *unperturbed propagator* $U_1^0(t)$ as the operator which, acting on the initial value of the RDF produces its value at time t:

$$f(\mathbf{q}_1, \mathbf{v}_1; t) = U_1^0(t)\, f(\mathbf{q}_1, \mathbf{v}_1; 0). \tag{5.12}$$

The propagator of Eq. (5.11) is formally written as $U_1^0(t) = \exp(L_1^0 t)$. Using Eq. (3.22), this formula becomes:

$$U_1^0(t) = \exp\left(-\mathbf{v}_1 \cdot \nabla_1\, t\right). \tag{5.13}$$

We substitute this result into (5.12) and recall the following identity defining the exponential of a differential operator:[4]

$$\exp\left(a\,\frac{d}{dx}\right) f(x) = f(x + a). \tag{5.14}$$

We then obtain the explicit solution of the initial value problem for the unperturbed RDF:

---

[4]This identity is easily proved by expanding both sides in a Taylor series.

$$f(\mathbf{q}_1, \mathbf{v}_1; t) = f(\mathbf{q}_1 - \mathbf{v}_1 t, \mathbf{v}_1; 0). \tag{5.15}$$

We note that this solution is in perfect agreement with Eq. (3.18): the phase space density at time t at point $(\mathbf{q}_1, \mathbf{v}_1)$ equals the density at time $t = 0$ at the point where the particle was located at that time: this position is determined by tracing the phase space point backwards in time t along the particle trajectory. The latter is here just a straight line motion with constant velocity $\mathbf{v}_1$.

The propagator of the equation (5.11) for the correlation function is just as easily obtained. As the Liouvillians L_1^0 and L_2^0 commute with each other, we obtain simply:

$$g_2(x_1, x_2; t) = U_{12}^0(t)\, g_2(x_1, x_2; 0), \tag{5.16}$$

with:

$$U_{12}^0(t) = \exp[(L_1^0 + L_2^0)t] = U_1^0(t)\, U_2^0(t). \tag{5.17}$$

5.3   The Vlasov Equation

We now start the perturbative treatment of the evolution. The purpose of our calculation should first be clearly stated. In elementary perturbation theory, (such as e.g. the calculation of the stationary wave function by solving the Schrödinger equation in quantum mechanics) the unknown function is expanded in a power series in the small parameter, and the coefficients of this series are determined by a systematic procedure, thus yielding more and more precise approximations of the unknown object. In the present problem this procedure leads to serious difficulties. Indeed, the coefficients of the expansion are functions of time which, typically, turn out to be *secular*, i.e. to be systematically growing functions (such as positive powers of t). As a result, the coefficient of any power of the small parameter (say, λ^p) becomes very large after long enough time, leading to a breakdown of the perturbation series, even though the complete function may be bounded in time [a trivial example is provided by the function $\exp(-\lambda t) = 1 - t\lambda + \frac{1}{2}t^2\lambda^2 + ...$: in spite of the smallness of λ, any truncated approximation blows up for time longer than λ^{-1} although the complete function is bounded for all times and tends to zero as $t \to \infty$]. This type of expansion, truncated to a finite number of terms, is only valid for times so short as to be irrelevant: in kinetic theory.

We shall be interested, on the contrary, in the behaviour of the systems for times that are very long compared to the characteristic microscopic times. In older treatments, the difficulty was overcome by writing down the formal expressions of the terms in the perturbation series, selecting and summing an infinite subseries of relevant terms (the most divergent ones in each order of λ), and deriving an equation for

this partial series. This rather cumbersome procedure can be short-circuited by *expanding the evolution operator* of the RDF rather than the unknown function. Thus, when we speak of the *kinetic theory "to order λ^n"* we mean that we consider *a theory based on a kinetic equation whose evolution operator is of order λ^n*. The RDF $f(x, t)$ in this approximation is obtained by solving this equation by any appropriate method; *this solution contains, of course, terms of all orders in λ*.

We now consider the classical equation of evolution (4.41) and analyze the terms by taking into account the weak coupling ordering (5.5) - (5.7). The right hand side contains a term of order λ ($\sim L'ff$) and a term of order λ^2 ($\sim L'g_2$). Thus, *the kinetic equation to order λ* is obtained by neglecting the second term:

$$\partial_t f(x_1; t) = L_1^0 f(x_1; t) + \int dx_2 \, L_{12}' f(x_1; t) f(x_2; t) . \tag{5.18}$$

In terms of diagrams, this equation is represented by the simple diagram of Fig. 5.1.
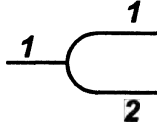
Figure 5.1: Diagram for the Vlasov Equation

A first feature is obvious: Eq. (5.18) is a *closed equation for the RDF $f(x; t)$*: there is no coupling to the higher order correlations in this order. In order to understand its physical meaning, we write explicitly the last term by using Eqs. (3.23) and (3.20):

$$\int dx_2 \, L_{12}' f(x_1; t) f(x_2; t) = m^{-1} \int dx_2 \, (\nabla_1 V_{12}) \cdot \partial_{12} f(x_1; t) f(x_2; t)$$

$$= m^{-1} \left\{ \nabla_1 \int d\mathbf{q}_2 d\mathbf{v}_2 \, V_{12}(\mathbf{q}_1 - \mathbf{q}_2) f(\mathbf{q}_2, \mathbf{v}_2; t) \right\} \cdot \partial_1 f(\mathbf{q}_1, \mathbf{v}_1; t) . \tag{5.19}$$

[In the last equation we replaced $\partial_{12} \equiv \partial_1 - \partial_2$ by ∂_1 because the term $\partial_2 f(x_2; t)$ yields a vanishing contribution after integration over $\mathbf{v}_2$, see Eq. (4.26)]. Eq. (5.18) will be written compactly as follows:

$$(\partial_t + \mathbf{v}_1 \cdot \nabla_1) \, f(\mathbf{q}_1, \mathbf{v}_1; t) = \mathcal{V} \{ f f \} , \tag{5.20}$$

with:

$$\mathcal{V}\{f\,f\} = m^{-1}\left\{\nabla_1 \int d\mathbf{q}_2 d\mathbf{v}_2\, V_{12}(\mathbf{q}_1 - \mathbf{q}_2)\, f(\mathbf{q}_2, \mathbf{v}_2; t)\right\} \cdot \partial_1 f(\mathbf{q}_1, \mathbf{v}_1; t)\,. \qquad (5.21)$$

The bracketted term in this equation has a clear physical meaning: it is the gradient of an *average interaction potential*. Indeed, the integral represents the value at the position $\mathbf{q}_1$ of the interaction with a particle 2, averaged over all positions in phase space of the latter. We thus introduce the average potential:

$$\overline{V}(\mathbf{q}_1; t) = \int d\mathbf{q}_2 d\mathbf{v}_2\, V_{12}(\mathbf{q}_1 - \mathbf{q}_2)\, f(\mathbf{q}_2, \mathbf{v}_2; t) \qquad (5.22)$$

Eq. (5.18) can thus also be written as follows:

$$(\partial_t + \mathbf{v} \cdot \nabla)\, f(\mathbf{q}, \mathbf{v}; t) = m^{-1}\left[\nabla \overline{V}(\mathbf{q}; t)\right] \cdot \partial f(\mathbf{q}, \mathbf{v}; t) \qquad (5.23)$$

This very celebrated equation is called the VLASOV EQUATION after the name of the Soviet physicist who derived it (semi-intuitively) in 1938. It has the form of the Liouville equation for *a set of **non-interacting** particles moving under the action of an **external** field* (3.22), (3.24). To this order of approximation, the effect of the interactions is simply to define an average field which influences the motion of the particles. It must be stressed, however, that the average potential is *self-consistent*: it is determined by the instantaneous value of the RDF through Eq. (5.22): as this function changes in time under the action of $\overline{V}(\mathbf{q}; t)$, the average potential itself is changing synchronously. As a result, the Vlasov equation is a NONLINEAR equation, as can be seen immediately from the form (5.18): the analogy with the linear Liouville equation in an "external" field is thus superficial.

An important feature that should be stressed at this point is the following: *the Vlasov equation determines a non-trivial evolution only for spatially inhomogeneous systems*. Consider, indeed, a spatially homogeneous system, for which the distribution function depends only on the velocity [see (4.20): $f(\mathbf{q}, \mathbf{v}; t) = n\varphi(\mathbf{v}; t)$. Then, clearly, $\nabla f = 0$. The average potential defined in (5.22) becomes:

$$\overline{V} = n \int d\mathbf{r}\, V(r)$$

[we used Eq. (4.22), and changed the integration variable $\mathbf{q}_2 \to \mathbf{r} = \mathbf{q}_1 - \mathbf{q}_2$]. The average potential is thus independent of $\mathbf{q}$, hence $\nabla \overline{V} = 0$. We thus find, for a spatially homogeneous system:

$$\partial_t \varphi(\mathbf{v}; t) = 0 + O(\lambda^2)\,. \qquad (5.24)$$

Thus, up to order λ, the velocity distribution of a spatially homogeneous system does not change in time.

We may note now that the Vlasov mean field is actually important only when the range of the interactions is long compared to the characteristic range of variation of the density gradient. We illustrate this feature with a simple one-dimensional example. Let the density profile [i.e. $n(x) = \int dv f(x, \mathbf{v})$] depend exponentially on x, and let the interaction potential have a similar dependence on the distance:

$$n(x) = n \exp(-x/l_H), \quad V(r) = V \exp\left[-|x_1 - x_2|/l_C\right] \tag{5.25}$$

The average potential $U(x)$ (in the region $0 < x < \infty$) is:

$$U(x) = \frac{1}{nV} \int_0^\infty dx' V(x - x') n(x')$$

$$= \frac{\exp(-x/l_H) - \exp(-x/l_C)}{l_C^{-1} - l_H^{-1}} + \frac{\exp(-x/l_H)}{l_C^{-1} + l_H^{-1}} . \tag{5.26}$$

Taking the characteristic length of the density gradient $l_H = 1$ as a reference, we show in Fig. 5.2 the function $U(x)$ for three values of the range of the interaction potential ($l_C = 1, 0.1, 0.01$). It is clearly seen that when the interaction range l_C is short compared to the density gradient length l_H, i.e. $l_C/l_H \ll 1$, the average Vlasov field becomes very small over the whole range of x. On the other hand, for long range interactions (such as the Coulomb potential that decays as an inverse power law, $V(r) \sim r^{-1}$, see the discussion of Sec. 2.4), the Vlasov term is very important.

The Vlasov equation is therefore a basic tool of *plasma physics*: because of the long range of the Coulomb interactions, the average potential acting on a given particle is effectively produced by a large number of charged particles. This explains the highly collective type of behaviour of plasmas. It is therefore useful to consider the specific application of the Vlasov equation to plasmas.

The main generalization needed in this case is the consideration of a multi-species system. We consider a simple fully ionized plasma consisting of N electrons (mass: m_e, charge: $e_e = -e$) and N singly charged positive ions (mass: m_i, charge: $e_i = +e$). The equal number of electrons and ions ensures the global electroneutrality: $Ne_i + Ne_e = 0$. The statistical description of the plasma now requires the specification of *two* RDF's: $f^\alpha(\mathbf{q}, \mathbf{v}; t)$, $\alpha = e, i$. (similarly, one has three correlation functions: $g_2^{\alpha\beta}(x_1, x_2; t)$, $\alpha = e, i$; $\beta = e, i$, etc.). The adaptation of the general formalism to this case is very easy and is left as an exercise for the reader; we go over to the final results. Eq. (5.18) becomes now:

$$\partial_t f^\alpha(x_1; t) = L_1^0 f^\alpha(x_1; t) + \sum_{\beta=e,i} \int dx_2 \, L_{12}^{\prime\alpha\beta} \, f^\alpha(x_1; t) f^\beta(x_2; t), \quad \alpha = e, i. \tag{5.27}$$

In the case of Coulomb interactions we have $V_{12}^{\alpha\beta}(r) = e_\alpha e_\beta / r$. (We use here the Gauss system of units for electromagnetic quantities, which is much more natural for
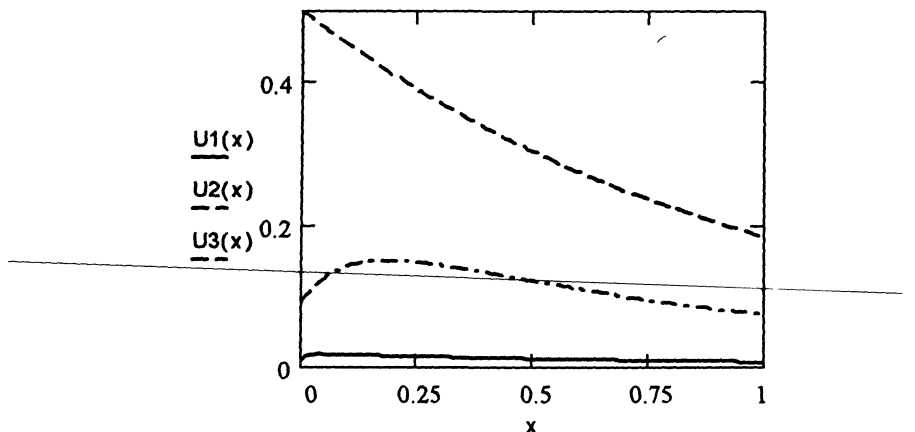
Figure 5.2: Average potential, for several values of $p = l_C/l_H$. Solid: $p = 0.01$, dash-dot: $p = 0.1$, dash: $p = 1$

a microscopic theory than the SI systems used by engineers). In order to be consistent with the usual electromagnetic notations, we write Eq. (5.19) in the following form:

$$\sum_{\beta=e,i} \int dx_2\, L_{12}'^{\alpha\beta}\, f^\alpha(x_1;t) f^\beta(x_2;t) = -\frac{e_\alpha}{m_\alpha} \overline{\mathbf{E}}(\mathbf{q}_1;t) \cdot \partial_1 f^\alpha(x_1;t)\,, \tag{5.28}$$

with:

$$\overline{\mathbf{E}}(\mathbf{q}_1;t) = -\nabla_1 \overline{\Phi}(\mathbf{q}_1;t)\,, \tag{5.29}$$

and:

$$\overline{\Phi}(\mathbf{q}_1;t) = \sum_\beta e_\beta \int d\mathbf{q}_2 d\mathbf{v}_2\, \frac{1}{|\mathbf{q}_1 - \mathbf{q}_2|}\, f^\beta(\mathbf{q}_2, \mathbf{v}_2;t)\,. \tag{5.30}$$

These results have a very simple interpretation. The mechanical force appearing in Eq. (5.28) is expressed in terms of an average electric field $\overline{\mathbf{E}}$, which in turn derives from an average scalar (electrostatic) potential $\overline{\Phi}$, defined by (5.30). The latter has exactly the form of the potential produced by a macroscopic charge density σ:

$$\sigma(\mathbf{q}_2;t) = \sum_\beta e_\beta \int d\mathbf{v}_2\, f^\beta(\mathbf{q}_2, \mathbf{v}_2;t)\,. \tag{5.31}$$

Clearly, the potential $\overline{\Phi}$ is a solution of the *Poisson equation*:

$$\nabla^2 \overline{\Phi}(\mathbf{q}; t) = -4\pi\sigma(\mathbf{q}; t) \,. \tag{5.32}$$

Thus, in the Vlasov picture, each particle feels the action of an average field produced by all the other particles. The latter act like a continuous "smeared-out" continuous charge distribution $\sigma(\mathbf{q}; t)$: they lost their discrete, point-like character in the process of averaging.

We note that to any particular solution of the Poisson equation can be added a solution of the homogeneous (Laplace) equation, Φ_0, representing the potential of an external field, i.e., a field produced by external sources. We may define a *total electric field*:

$$\mathbf{E} = \mathbf{E}_0 + \overline{\mathbf{E}} = -\nabla\left(\Phi_0 + \overline{\Phi}\right) \equiv -\nabla\Phi, \tag{5.33}$$

which obeys the Poisson equation with appropriate boundary conditions. The Vlasov equation is finally written in the form:

$$\partial_t f^\alpha(\mathbf{q}, \mathbf{v}; t) = -\mathbf{v} \cdot \nabla f^\alpha(\mathbf{q}, \mathbf{v}; t) - \frac{e_\alpha}{m_\alpha} \mathbf{E}(\mathbf{q}; t) \cdot \partial f^\alpha(\mathbf{q}, \mathbf{v}; t). \tag{5.34}$$

This equation is coupled to the Poisson equation:

$$\nabla \cdot \mathbf{E}(\mathbf{q}; t) = 4\pi \sum_\beta e_\beta \int d\mathbf{v} \, f^\beta(\mathbf{q}, \mathbf{v}; t), \tag{5.35}$$

together with the constraint:

$$\nabla \wedge \mathbf{E}(\mathbf{q}; t) = 0 \,. \tag{5.36}$$

Eqs. (5.34) - (5.36) constitute a closed set of equations allowing the determination of the distribution functions f^α . The nonlinear character of these equations make them very difficult, but also extremely rich: a considerable part of plasma physics is based on them.

5.4   The Linearized Vlasov Equation

In order to gain insight into the physics contained in the Vlasov equation, we consider a simplified form, obtained by linearization around a given spatially homogeneous reference state depending only on the absolute value of the velocity [we know that any such function is a stationary solution of the Vlasov equation, see (5.24]. We thus assume that the RDF has the following form:

$$f^\alpha(\mathbf{q}, \mathbf{v}; t) = n \, \varphi_0^\alpha(v) + \delta f^\alpha(\mathbf{q}, \mathbf{v}; t) \,, \tag{5.37}$$

(where n is the constant, unperturbed number density of both species) and assume:

$$\delta f^\alpha(\mathbf{q}, \mathbf{v}; t) \ll n\, \varphi_0^\alpha(v)\,. \tag{5.38}$$

[Note the difference in the strategy as compared to the discussion at the beginning of Sec. 5.3: we are now seeking a *solution* to a given equation of evolution by a true perturbation method. The small parameter here is no longer the interaction strength λ, but rather the "distance" between the true solution and the reference state]. The linearization of Eq. (5.34), combined with (5.33), is straightforward:

$$\partial_t \delta f^\alpha(\mathbf{q}, \mathbf{v}; t) + \mathbf{v} \cdot \nabla \delta f^\alpha(\mathbf{q}, \mathbf{v}; t) = \frac{e_\alpha}{m_\alpha}\, n\, [\nabla \Phi(\mathbf{q}; t)] \cdot \partial \varphi_0^\alpha(v)\,; \tag{5.39}$$

this equation is coupled to the Poisson equation (5.32) for the total potential (possibly including an external potential):

$$\nabla^2 \Phi(\mathbf{q}; t) = -4\pi \sum_\beta e_\beta \int d\mathbf{v}\, \delta f^\beta(\mathbf{q}, \mathbf{v}; t)\,. \tag{5.40}$$

These equations are easily solved by performing a Fourier transform of the unknown functions with respect to $\mathbf{q}$, and a Laplace transform (or, a one-sided Fourier transform) with respect to time. We thus define:

$$\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z) = \frac{1}{(2\pi)^3} \int d\mathbf{q}\, e^{-i\mathbf{k} \cdot \mathbf{q}} \int_0^\infty dt\, e^{izt}\, \delta f^\alpha(\mathbf{q}, \mathbf{v}; t)\,. \tag{5.41}$$

Here z is to be considered as a complex variable[5]. The inversion formula for the Laplace transform involves an integration over the well-known Bromwich contour Γ in the complex z-plane passing above all the singularities of the function $\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z)$:

$$\delta f^\alpha(\mathbf{q}, \mathbf{v}; t) = \int d\mathbf{k}\, e^{i\mathbf{k} \cdot \mathbf{q}} \frac{1}{2\pi} \int_\Gamma dt\, e^{-izt}\, \delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z)\,. \tag{5.42}$$

Similar definitions hold for the Fourier-Laplace transform of the potential, $\widehat{\Phi}(\mathbf{k}; z)$. Eqs. (5.39), (5.40) are transformed as follows:

$$(-iz + i\mathbf{k} \cdot \mathbf{v})\, \delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z) = \frac{e_\alpha}{m_\alpha} n\, \widehat{\Phi}(\mathbf{k}; z)\, i\mathbf{k} \cdot \partial \varphi_0^\alpha(v) + \delta f^\alpha(\mathbf{k}, \mathbf{v}; 0)\,, \tag{5.43}$$

---

[5]The more usual notation for the complex Laplace variable is $s = -iz$. The choice made here introduces more symmetry with the Fourier transformation (this is why it is sometimes called a one-sided Fourier transform). The passage from one system of notations to the other is very easy. In particular, the Bromwich contour for the inversion of the Laplace transform, defined as a vertical line to the right of all singularities in the s-plane, becomes a horizontal line above all singularities in the z-plane. The more familiar "s-form" of the Laplace transform will be used in Chap. 12.

$$k^2 \widehat{\Phi}(\mathbf{k}; z) = 4\pi \sum_\beta e_\beta \int d\mathbf{v}\, \delta \widehat{f}^\beta(\mathbf{k}, \mathbf{v}; z). \tag{5.44}$$

Here $\delta f^\alpha(\mathbf{k}, \mathbf{v}; 0)$ is the initial value of the spatial Fourier transform of the RDF, $\delta f^\alpha(\mathbf{k}, \mathbf{v}; t = 0)$. The purely algebraic equation (5.43) is immediately solved:

$$\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z) = \frac{1}{i(\mathbf{k} \cdot \mathbf{v} - z)} \left[\frac{e_\alpha}{m_\alpha} n\, \widehat{\Phi}(\mathbf{k}; z)\, i\mathbf{k} \cdot \partial \varphi_0^\alpha(v) + \delta f^\alpha(\mathbf{k}, \mathbf{v}; 0) \right]. \tag{5.45}$$

This equation introduces the RESOLVENT $R_1^0(z)$ of the unperturbed Liouvillian, which is nothing other than the Fourier-Laplace transform of the propagator $U_1^0(t)$, Eq. (5.13):

$$R_1^0(z) = \frac{1}{i(\mathbf{k} \cdot \mathbf{v} - z)}. \tag{5.46}$$

The result (5.45) is now substituted into the Poisson equation (5.44):

$$\widehat{\Phi}(\mathbf{k}; z) = \sum_\beta \frac{4\pi e_\beta^2 n}{m_\beta k^2} \widehat{\Phi}(\mathbf{k}; z) \int d\mathbf{v}\, \frac{i\mathbf{k} \cdot \partial \varphi_0^\beta(v)}{i(\mathbf{k} \cdot \mathbf{v} - z)} + \frac{4\pi}{k^2} \sum_\beta e_\beta \int d\mathbf{v}\, \frac{\delta f^\beta(\mathbf{k}, \mathbf{v}; 0)}{i(\mathbf{k} \cdot \mathbf{v} - z)}. \tag{5.47}$$

We now introduce two important quantities. The *plasma frequency* (also called the *Langmuir frequency*) $\omega_{p\alpha}$ of species α is defined as:

$$\omega_{p\alpha}^2 = \frac{4\pi e_\alpha^2 n}{m_\alpha}; \tag{5.48}$$

for a given species, it is a function of the density n. Next, we define the *dielectric function* of the plasma as:

$$\varepsilon(\mathbf{k}; z) = 1 - \sum_\alpha \frac{\omega_{p\alpha}^2}{k^2} \int d\mathbf{v}\, \frac{\mathbf{k} \cdot \partial \varphi_0^\alpha(v)}{\mathbf{k} \cdot \mathbf{v} - z} \tag{5.49}$$

This functional of $\varphi_0^\alpha(v)$ characterizes the unperturbed state of the plasma. The solution of Eq. (5.47) is now written as follows:

$$\widehat{\Phi}(\mathbf{k}; z) = \frac{4\pi}{k^2 \varepsilon(\mathbf{k}; z)} \sum_\beta e_\beta \int d\mathbf{v}\, \frac{\delta f^\beta(\mathbf{k}, \mathbf{v}; 0)}{i(\mathbf{k} \cdot \mathbf{v} - z)}. \tag{5.50}$$

This solution for the potential is substituted back into (5.43), with the result:

$$\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z) = \frac{\delta f^\alpha(\mathbf{k}, \mathbf{v}; 0)}{i(\mathbf{k} \cdot \mathbf{v} - z)} + \frac{4\pi n e_\alpha}{m_\alpha k^2} \frac{\mathbf{k} \cdot \partial \varphi_0^\alpha(v)}{(\mathbf{k} \cdot \mathbf{v} - z)\, \varepsilon(\mathbf{k}; z)} \sum_\beta e_\beta \int d\mathbf{v}'\, \delta f^\beta(\mathbf{k}, \mathbf{v}'; 0). \tag{5.51}$$

This is the *exact solution of the initial value problem for the linearized Vlasov equation*.It is conveniently written in terms of a RESOLVENT *operator* that connects $\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z)$ to the initial value:[6]

$$\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z) = \sum_\beta \int d\mathbf{v}' \, R_{VL}^{\alpha\beta}(\mathbf{v}|\mathbf{v}'; \mathbf{k}; z) \, \delta f^\beta(\mathbf{k}, \mathbf{v}'; 0) \,. \tag{5.52}$$

Comparing with (5.51), we find:

$$R_{VL}^{\alpha\beta}(\mathbf{v}|\mathbf{v}'; \mathbf{k}; z) = \frac{1}{i\,(\mathbf{k} \cdot \mathbf{v} - z)} \delta^{\alpha\beta}\delta(\mathbf{v} - \mathbf{v}') + \frac{4\pi n e_\alpha e_\beta}{m_\alpha \, k^2} \frac{\mathbf{k} \cdot \partial \varphi_0^\alpha(v)}{(\mathbf{k} \cdot \mathbf{v} - z)\, \varepsilon(\mathbf{k}; z)} \,. \tag{5.53}$$

The knowledge of the resolvent provides us with valuable information about the type of time dependence of the solution of the linearized Vlasov equation. Indeed, the inverse Laplace transform of $\delta \widehat{f}^\alpha(\mathbf{k}, \mathbf{v}; z)$ is calculated by determining the poles z_p of the integrand in Eq. (5.42) and calculating the residues r_p at these poles; we then have, by the theorem of residues:

$$\delta \widetilde{f}^\alpha(\mathbf{k}, \mathbf{v}; t) = \sum_p (2\pi i) r_p \, e^{-iz_p t} \,. \tag{5.54}$$

[We assumed here, for simplicity, that the only singularities of the resolvent are simple poles]. A mere glance at Eq. (5.53) shows that there are two kinds of poles. We immediately recognize the real pole $z_p = \mathbf{k} \cdot \mathbf{v}$: it is clearly related to the *free motion* part of the Liouvillian. It produces an undamped oscillation of the Fourier transform of the RDF; its frequency is proportional to the velocity of the particle. It is therefore typically an *individual particle* effect. An interesting quantity is the *density profile* $\delta \widetilde{n}^\alpha(\mathbf{q}; t)$ of the perturbation, or its Fourier transform:

$$\delta \widetilde{n}^\alpha(\mathbf{k}; t) = \int d\mathbf{v} \, \delta \widetilde{f}^\alpha(\mathbf{k}, \mathbf{v}; t) \tag{5.55}$$

Clearly, the contribution to this integral from the various velocities will produce destructive interferences of the oscillations $\exp(-i\mathbf{k} \cdot \mathbf{v}t)$, hence this part of $\delta \widetilde{n}^\alpha(\mathbf{k}; t)$ tends to zero for long times: this is the phenomenon of *phase mixing*.

The resolvent (5.53) possesses another set of poles: they correspond to the zeroes of the dielectric function:

$$\varepsilon(\mathbf{k}; z_p) = 0 \,. \tag{5.56}$$

---

[6]Note that, in contrast to the simple unperturbed Liouvillian resolvent, the Vlasov resolvent is no longer a mere function of $\mathbf{v}$, (i.e., a diagonal operator), but rather a non-trivial operator, represented by a matrix (or integral kernel).

This *dispersion equation* determines a set of roots $z_p = z_p(\mathbf{k})$ that depend on $\mathbf{k}$, but *not* on $\mathbf{v}$. Their location in the complex plane is determined by the *unperturbed* RDF. These roots represent an intrinsic property of the background plasma: they describe the characteristic *collective behaviour* of these systems. In many cases, and in particular, in thermal equilibrium, these roots are located on or below the real axis: such a plasma state is called *linearly stable*. The long time behaviour of the density profile is determined by the roots located closest to the real axis: they produce a *weakly damped oscillation* that "resists the integration over $\mathbf{v}$".

We illustrate these statements with a specific simple example. We consider a "one-component plasma": the ions are modeled by a continuous background that plays no role in the dynamics and whose effect is merely to neutralize the total charge of the electrons. Eq. (5.51) then reduces to:

$$\delta\widehat{f}(\mathbf{k},\mathbf{v};z) = \frac{\delta f(\mathbf{k},\mathbf{v};0)}{i\,(\mathbf{k}\cdot\mathbf{v}-z)} + \frac{\omega_{pe}^2}{k^2}\frac{\mathbf{k}\cdot\partial\varphi_0(v)}{(\mathbf{k}\cdot\mathbf{v}-z)\,\varepsilon(\mathbf{k};z)}\int d\mathbf{v}'\,\delta f(\mathbf{k},\mathbf{v}';0)\,, \qquad (5.57)$$

where ω_{pe} is the electron *plasma frequency* defined in Eq. (5.48). We now consider a background electron distribution function of the following form:[7]

$$\varphi_0(v) = \frac{1}{\pi^2 u_0^3}\frac{1}{\left(1+\dfrac{v^2}{u_0^2}\right)^2}. \qquad (5.58)$$

The initial deviation from the reference state is assumed to have a similar form:

$$\delta f(\mathbf{k},\mathbf{v};0) = \frac{F(\mathbf{k})}{\pi^2 w_0^3}\frac{1}{\left(1+\dfrac{(\mathbf{v}-\mathbf{v}_0)^2}{w_0^2}\right)^2}\,, \qquad (5.59)$$

where the function $F(\mathbf{k})$ is sharply peaked (it defines a wave packet), but its exact shape is not relevant here. Combining Eqs. (5.49), (5.56) and (5.58), the dispersion equation is written explicitly by performing the velocity integration by the method of residues (with z_p lying in the upper half-plane):

$$\varepsilon(\mathbf{k},z_p) = 1 + \frac{\omega_{pe}^2}{\pi^2 u_0^3 k^2}\int d\mathbf{v}\,\frac{4\mathbf{k}\cdot\mathbf{v}}{u_0^2\left(1+\dfrac{v^2}{u_0^2}\right)^2(\mathbf{k}\cdot\mathbf{v}-z_p)}$$

---

[7]A more realistic case would be to consider for φ_0 a Maxwellian distribution. In that case, however, the integrations cannot be done analytically. The dielectric constant is expressed in terms of a transcendental function, called the "plasma dispersion function"; the latter is tabulated and widely used in plasma physics. The function chosen in Eq. (5.58) yields a dielectric function having the same qualitative features as the maxwellian dielectric function.

$$= \ 1 - \frac{\omega_{pe}^2}{k^2}\frac{1}{\left(iu_0 + \frac{z_p}{k}\right)^2} = 0. \tag{5.60}$$

(This function is continued analytically into the lower half plane of z_p, where it keeps the same form). The roots of the dispersion equation are thus:

$$z_p = \pm\omega_{pe} - iku_0. \tag{5.61}$$

Finally, we use these results in Eq. (5.51), from which we calculate the density profile (5.55) and finally perform the inverse Laplace transform, obtaining:

$$\begin{aligned}
\delta n(\mathbf{k}, t) \ = \ & F(\mathbf{k})\left\{e^{-i\mathbf{k}\cdot\mathbf{v}_0 t - kw_0 t}\left[1 + \frac{\omega_{pe}^2}{\left[\mathbf{k}\cdot\mathbf{v}_0 + ik\left(u_0 - w_0\right)\right]^2 - \omega_{pe}^2}\right]\right. \\
& \left. + \frac{\omega_{pe}}{2}e^{-ku_0 t}\left[\frac{e^{-i\omega_{pe}t}}{\mathbf{k}\cdot\mathbf{v}_0 + ik(u_0 - w_0) - \omega_{pe}} - \frac{e^{i\omega_{pe}t}}{\mathbf{k}\cdot\mathbf{v}_0 - ik(u_0 - w_0) - \omega_{pe}}\right]\right\}.
\end{aligned}$$
$$\tag{5.62}$$

The exponential in the first term originates from the pole in $z = \mathbf{k}\cdot\mathbf{v}$; its complex frequency is entirely determined by the characteristics of the initial condition (5.59): it is not an intrinsic property of the background plasma. It contains a damping coefficient kw_0, depending on the width of the initial velocity perturbation. This damping describes the dispersion of the initial wave packet (which moves with the average velocity $\mathbf{v}_0$) by phase mixing. The second term is very different: it describes a "true" wave, with a characteristic frequency ω_{pe} which is a constant depending only on the density of the background plasma ($\omega_{pe} \sim \sqrt{n}$). This term represents a collective motion, called a *plasma wave*, or *Langmuir wave*. It represents physically the reaction of the plasma to a disturbance producing a local charge unbalance: the electrons rush back to their equilibrium position and start an oscillatory motion with frequency ω_p. The Langmuir waves are damped by a mechanism called *Landau damping*, which affects mainly the short wavelength components. We refer the reader to any treatise of plasma physics for further details about the large variety of collective wave motions that exist in a plasma in realistic situations (in particular, in presence of external magnetic fields). For the study of these complex motions, which can make the plasma unstable, the Vlasov equation is the basic tool.

5.5   Conclusions.

The equation of evolution obtained in the present chapter possesses several important features.

- It is derived as a *first order approximation in an expansion of the evolution equation of the RDF in powers of the interaction strength* λ.

- To this order of approximation, *the correlations are completely decoupled from the RDF*. It is easily seen that the correlation function $g_2(x_1, x_2; t)$, which is of order λ, obeys simply the unperturbed equation of motion. Hence, there is no creation or destruction of correlations in this process.

- The physical picture of the evolution process is very simple. *The interactions are self-consistently averaged and produce an average potential.* The individuality of the point particles is smeared out: they appear as a *quasi-continuous background.* Each particle moves under the action of this *mean field* which, formally, acts as an "external" field.

- The concept of a mean field as described above only makes sense in a system containing a very large number of particles, in which the local, intensive physical quantities (such as the particle density) are well defined. Specifically, it is assumed that the *thermodynamic limit* (4.19) has been taken from the very beginning in dealing with the BBGKY hierarchy.

- The Vlasov equation clearly describes the *collective aspects of the interactions*, i.e., those which involve simultaneous and synchronized actions of a large number of particles. This is why this equation is particularly important for describing long range interactions, such as the Coulomb interactions characterizing fully ionized *plasmas*.

- The Vlasov equation *reduces to the trivial form* $\partial_t f = 0$ *for spatially homogeneous systems*. Thus, the equation describes no relaxation of an arbitrary initial velocity distribution towards a state of thermal equilibrium.

- For all these reasons, the Vlasov equation does not contain a description of the individual particle collisions. These will appear in higher order approximations, as will be seen in forthcoming chapters. The Vlasov equation should therefore NOT be called a "kinetic equation" [8] in the strict sense, a term that will be defined in our subsequent developments. We will rather call it a MEAN FIELD EQUATION.

5.6   Bibliographical Notes BN5

The first "derivation" of the Vlasov equation was given in:

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[8] Although many authors do so!

Vlasov, A.A., 1938, Zh. Eksp. Teor. Fiziki, **8**, 291.

True derivations were given by:

Bogolioubov, N.N., 1946, *Problems of a Dynamical Theory in Statistical Physics* (in russian); English translation in: *Studies in Statistical Mechanics* (J. de Boer and G.E. Uhlenbeck, eds.), vol. **1**, p. 5, North Holland, Amsterdam, 1962, **RB-1** (see **BN1**).

A derivation from the BBGKY hierarchy in the mathematical limit: $e \to 0$, $m \to 0$, $n \to \infty$, with the conditions $e/m = const$, $en = const$ was given by:

Rostoker, N. and Rosenbluth, M.N., 1960, Phys. Fluids, **3**, 1.

There exists an enormous amount of literature on the Vlasov equation: practically all books on plasma physics contain a more or less detailed description of its properties. We only quote here a few relatively recent general textbooks:

Akhiezer, A.I., Akhiezer, I.A., Polovin, R.V., Sitenko, A.G. and Stepanov, K.N., 1975, *Plasma Electrodynamics*, (2 vols.), Pergamon, Oxford,

Golant, V.E., Zhilinsky, A.P. and Sakharov, I.E., 1980, *Fundamentals of Plasma Physics*, Wiley, New York,

Nicholson, D., 1983, *Introduction to Plasma Physics*, Wiley, New York,

Cairns, R.A., 1985, *Plasma Physics*, Blackie, Glasgow,

Ichimaru, S., 1992, *Statistical Plasma Physics*, (vol. 1), 1992, Addison-Wesley, New York,

Krall, N.A. and Trivelpiece, A.W., 1973, *Principles of Plasma Physics*, McGraw Hill, New York; (reprint: 1986, San Francisco Press, San Francisco),

Dendy, R.O., 1990, *Plasma Dynamics*, Clarendon, Oxford,

Delcroix, J.L. and Bers, A., 1994, *Physique des Plasmas*, (2 vols.), InterEditions, Paris.

The plasma dispersion function is extensively tabulated in:

Fried, B.D. and Conte, S.D., 1961, *The Plasma Dispersion Function*, Academic Pr., New York.

The Weak Coupling Kinetic Equation

6.1 The Master Equation

The Vlasov equation, in spite of its importance in describing a certain type of collective phenomena, yields only a smeared-out picture of the many-body system, in which any given particle feels the effect of a quasi-continuous medium, acting on it in the same way as a field governed by the laws of macroscopic physics (e.g., Maxwell's equations). In order to explain the peculiar behaviour of many-body systems, in particular the intriguing *irreversibility of the evolution*, a more complete description of the motion of truly individual particles, involving the effect of their mutual encounters or *collisions* is needed. As will be seen in the present section, an equation of evolution valid to the next order of approximation for a weakly coupled system will provide us precisely with the missing elements.

We consider a classical weakly coupled system and derive the equation of evolution for the RDF $f(x_1; t)$ to second order in λ. We return to Eq. (4.41) and analyze the ... in view of the ordering (5.5) - (5.7). In addition to the terms retained in the ... approximation we must also keep now the last term in the right hand side ...

$$\int dx_2 \, L'_{12} \, f(x_1; t) f(x_2; t) + \int dx_2 \, L'_{12} \, g_2(x_1, x_2; t). \qquad (6.1)$$

... appearing here is the *coupling of the RDF to* ... this equation, we need to take into account ... equations, (4.44). We note that ... function correct to order ... only the first term

in the right hand side ($\sim L'ff$) is of order λ, all the others being of higher order ($L'g_2 \sim L'fg_2 \sim \lambda^2$, $L'g_3 \sim \lambda^3$). Thus, to the required order, Eq. (4.44) reduces to:

$$\left(\partial_t - L_1^0 - L_2^0\right) g_2(x_1, x_2; t) = L'_{12} f(x_1; t) f(x_2; t). \tag{6.2}$$

In terms of the graphical representation of Fig. 4.2, a single graph is kept in the present approximation, as shown in Fig. 6.1:
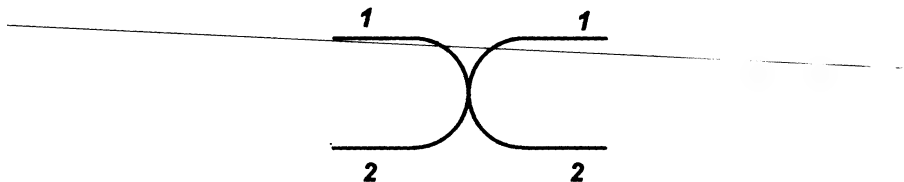
Figure 6.1: Diagram for the evolution of the correlation function $g_2(1, 2)$; weak coupling approximation

Eqs. (6.1), (6.2) constitute a closed set of equations for the two unknown functions f, g_2. Our strategy consists of solving (6.2) for g_2 and substituting the result into (6.1) in order to obtain a closed equation for f.

Eq. (6.2) has a very simple structure: it is an *unperturbed* Liouville equation of the form (5.11), to which a *source term* (independent of g_2) is added in the right hand side. Its solution is obtained in terms of the two-particle unperturbed propagator $U_{12}^0(t)$ as in Eq. (5.16), with an additional term involving a convolution of the propagator with the source term:

$$\begin{aligned} g_2(x_1, x_2; t) &= U_{12}^0(t)\, g_2(x_1, x_2; 0) \\ &+ \int_0^t d\tau\, U_{12}^0(\tau)\, L'_{12}\, f(x_1; t - \tau) f(x_2; t - \tau). \end{aligned} \tag{6.3}$$

We thus obtained an expression of the correlation function as a *functional of the RDF* f. Our programme is completed by substituting (6.3) into (6.1), with the result:

$$\begin{aligned} \left(\partial_t - L_1^0\right) f(x_1; t) &= \int dx_2\, L'_{12}\, f(x_1; t) f(x_2; t) + \int dx_2\, L'_{12}\, U_{12}^0(t)\, g_2(x_1, x_2; 0) \\ &+ \int dx_2 \int_0^t d\tau\, L'_{12} U_{12}^0(\tau)\, L'_{12}\, f(x_1; t - \tau) f(x_2; t - \tau). \end{aligned} \tag{6.4}$$

This is the exact equation of evolution for the weakly coupled classical system, obtained from Eqs. (6.1), (6.2) without any approximation. It is a special case of the general MASTER EQUATION derived by Prigogine and Résibois in 1961 (using a diagram technique). It contains, besides the Vlasov term which we already know, two new terms which have some unusual features. The second term in the right hand side is a functional of the *initial value of the correlation function*. It is indeed surprising that the rate of change of the RDF at a time t, which may be quite long, should be influenced by the value of the correlation (an "extraneous" quantity) at time $t = 0$. The last term is less surprising, although it has an "unusual" form: It tells us that the rate of change of the RDF at time t depends not only on the instantaneous state of the system at that time, but rather on the whole history of f from time $t = 0$ up to t. ~~Because of this feature, the master equation is called a NON-MARKOVIAN EQUATION.~~ This property is not unreasonable: it appears likely that the state in the near past could influence the events at time t; on the other hand the kernel in the convolution would be expected to be a rapidly decaying function of τ which would effectively cut off the influence of the remote past. Nevertheless, if Eq. (6.4) is used for deriving the macroscopic equations of hydrodynamics, this non-Markovian feature would be transmitted to the latter, and this would *not* correspond to the known equations [see Eqs. (2.2) - (2.7)]. We therefore have the feeling that some element is still missing in the analysis of Eq. (6.4): actually, we have not yet fully exploited the concept of weak coupling.

6.2   The Landau Equation

In order to gain insight, we should realize that there exist a number of characteristic time scales and length scales associated with our system. Actually, to each time scale, say T, corresponds a length scale L defined as $L = VT$, where V is a typical particle velocity, say the thermal velocity (here we are interested in orders of magnitude, not in exact values). In order to understand the role and the mutual relationships of these scales, we start the discussion with a qualitative analysis of the evolution.

In the Vlasov approximation the individuality of the particles was completely smeared out in the definition of the mean field. To the next order in λ, the general picture changes drastically. The evolution appears to be driven by a succession of interaction events that are *localized in space and time*. This interpretation is justified by the occurrence of the correlation function g_2 in the equations of evolution. As follows from the discussion of Sec. 5.1, this function has a finite range in space, hence in time. Consider a particle P, initially far away from all others: it moves uniformly along a straight line until it approaches another particle Q. The interaction forces particle P to deviate from its initial straight line into a curved path, whose shape depends on the position of its partner: the motion of P is now *correlated* to the

motion of Q. This mutual influence can only act as long as the distance between P and Q is smaller than the interaction (or correlation) range l_C defined in Eq. (5.8). The interaction event is thus *localized* in space in a region of size l_C: it is called a COLLISION. Correspondingly, this localized correlation only lasts for a finite time, adequately called the *duration of a collision*, τ_C, i.e., the time it takes an average particle to cross the correlation length. l_C and τ_C constitute a first pair of characteristic scales: they are assumed to be finite quantities ($\neq 0$, $< \infty$), independent of λ.[1] The occurrence of g_2 alone in Eqs. (6.1), (6.2) implies that only two-body collisions contribute significantly to the evolution. Three-body or higher-order collisions, associated with g_3, g_4, ..., play a negligible role in a weakly coupled system.

After a collision event, particle P continues its motion along a (new) straight orbit until it feels the action of a new particle R: at this moment starts a new collision event. The average length of the straight path between two successive collisions is very long when the density and the interaction strength are small. We thus see the emergence of a second characteristic length: the *mean free path*, l_{mfp}, which depends on λ. The corresponding average time between two successive collisions is called the *relaxation time*, τ_R; it is also interpreted as the inverse of the *collision frequency*. The latter quantity is measured by the last term in Eq. (6.1), i.e., the contribution of the correlations to the rate of change of f: it is a quantity of order λ^2.

The following subtle point should be noted here. The assumption of a finite small correlation scale can actually be realized only in a *very large system*. In the extreme opposite case, imagine a system of three particles. These particles continuously collide together, hence they remain correlated forever, $\tau_C = \infty$. On the contrary, in a very large system there is an enormous reservoir of particles. The probability of a recollision of two given particles (say: P and Q) is completely negligible.

Finally, there exists a third, independent length scale l_H, which measures the rate of spatial variation of the RDF in an inhomogeneous system; it is related to the local gradients of density, temperature, etc. It is defined (in order of magnitude) by:

$$l_H^{-1} \approx Max \left(\frac{1}{f} |\nabla f| \right) . \tag{6.5}$$

This *hydrodynamic length* depends generally on the macroscopic preparation of the system: it is thus of the order of the size of the apparatus (e.g., millimeters or centimeters in laboratory experiments), hence usually (but not always!) much larger than the two other characteristic lengths. Associated with l_H there is a *hydrodynamic time* t_H. We collect all these characteristic scales in the following table:

---

[1] In Sec. 2.4 it was pointed out that any "usual" interaction potential can be characterized by a parameter measuring its strength and a parameter measuring its range: these two quantities are mutually independent.

correlation length	l_C	τ_C	duration of collision
mean free path	l_{mfp}	τ_R	relaxation time	(6.6)
hydrodynamic length	l_H	τ_H	hydrodynamic time

We now formulate a *specific assumption* about the relative size of these parameters. The first assumption is:

$$\frac{l_C}{l_{mfp}} = O(\lambda^2)\,, \quad \frac{\tau_C}{\tau_R} = O(\lambda^2)\,. \tag{6.7}$$

This ordering follows from the smallness of the interaction strength and the finiteness of the interaction range, according to the previous discussion.

Next, we assume the following ordering for the hydrodynamic quantities:

$$\frac{l_{mfp}}{l_H} \equiv \lambda_H \ll 1\,, \quad \frac{\tau_R}{\tau_H} = \lambda_H \ll 1\,. \tag{6.8}$$

This ratio introduces a new dimensionless parameter λ_H. The assumption (6.8) defines a specific *hydrodynamic regime*: it covers an important range of experimental situations and gives rise to the so-called *classical transport theory*. It should be realized that there exist physically accessible situations where this ordering is not satisfied. For instance, in plasmas at very high temperatures (e.g., in controlled thermonuclear fusion conditions, $T \approx 10^8\ {}^0 K$) the mean free path becomes very long, of the order of meters. In an ordinary gas there may exist a shock wave in which the gradients of temperature and density are extremely steep in a small region of space: this is another instance of non-hydrodynamic regime. These problems will not be discussed here.

Summing up this discussion, in the weak coupling, hydrodynamic regime assumed here the following ordering of characteristic scales holds true:

$$l_C \ll l_{mfp} \ll l_H\,, \quad \tau_C \ll \tau_R \ll \tau_H\,. \tag{6.9}$$

In this problem, the scales are very widely separated. In most cases of physical interest, the duration of a collision τ_C is so short as to be inaccessible to measurement[2]. As a result, details of the evolution process occurring on time scales of order τ_C or spatial wiggles on scales of order l_C are irrelevant, because they are well below the threshold of sensitivity of the macroscopic apparatus. The time t of interest in kinetic theory will thus always be assumed to be much longer than the shortest characteristic time:

$$\tau_C \ll t\,. \tag{6.10}$$

---

[2]One often speaks in elementary kinetic theory of *instantaneous collisions*. In the hard sphere model, Eq. (2.35) the duration of a collision is strictly zero.

When studying the relaxation to equilibrium, e.g. in a homogeneous system (where $l_H = \infty$), we are interested in times of the order of the relaxation time $t \sim \tau_R$; in transport problems, we are interested in longer times: $t \sim \tau_H$. In any case, the assumption (6.10) means that for a physically relevant theory we are entitled to construct an ASYMPTOTIC DESCRIPTION of the evolution process.

We now return to the master equation (6.4) and continue its analysis by making use of the assumptions (6.7) - (6.10). We begin with the second term in the right hand side. We change the variable q_2 to the relative distance $r_{21} = q_2 - q_1$ in the correlation function (as was done in Sec. 5.3) and use Eqs. (5.13) - (5.17):

$$\int dx_2 \, L'_{12} \, U^0_{12}(t) \, g_2(x_1, x_2; 0)$$

$$= \int dr_{21} \int dv_2 \, L'_{12} \, U^0_{12}(t) \, g_2(q_1, r_{21}, v_1, v_2; 0)$$

$$= \int dr_{21} \int dv_2 \, L'_{12} \, g_2(q_1 - v_1 t, r_{21} - g_{21} t, v_1, v_2; 0). \qquad (6.11)$$

We introduced here the following notation for the *relative velocity* of two particles:

$$g_{jn} = v_j - v_n. \qquad (6.12)$$

We note that the second argument of the correlation function, $r_{21} - g_{21} t$, is an increasing function of time (in absolute value). Recalling our assumption (6.10), we see that the correlation function appearing in the last term ends up tending to zero after a finite time, such that $|r_{21} - g_{21} t| \gg l_C$. This is typically the time necessary for an average particle to cross the correlation zone, i.e., τ_C (see Fig. 6.2).
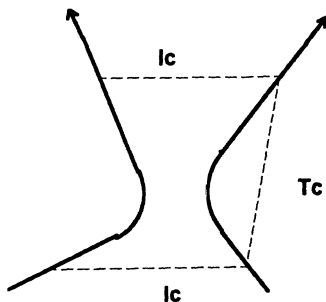
Figure 6.2: Correlation length and correlation time.

In conclusion, the term under consideration describes a *transient process* whose effective duration is τ_C:

$$\int dx_2 \, L'_{12} \, U^0_{12}(t) \, g_2(x_1, x_2; 0) \approx 0 \quad for \; t \gg \tau_C \, . \tag{6.13}$$

Hence, in the asymptotic limit (6.10), this term is negligibly small. This conclusion is physically quite clear: the initial correlations can influence the evolution process only for a finite time of order τ_C. Prigogine and Résibois picturesquely called this term: the *destruction term*, because it describes the "destruction" of the effect of the initial correlations on the evolution of the RDF.

We now analyze the last term in Eq. (6.4). Note that the retarded RDF's appearing here can be related to $f(t)$ by means of the propagator associated with Eq. (6.4). As we are interested in terms of order λ^2, and as there are already two operators L' in the integrand, the propagator can be approximated by its unperturbed form U^0:

$$
\begin{aligned}
f(x_1; t - \tau) f(x_2; t - \tau) &= U_{12}(-\tau) \, f(x_1; t) f(x_2; t) \\
&\approx U^0_{12}(-\tau) \, f(x_1; t) f(x_2; t) \, .
\end{aligned} \tag{6.14}
$$

We now write down explicitly the operators L' using (3.23), and the propagator U^0 using (5.13), (5.17) and perform the displacements [we use here the relative variables $r_{12} = q_1 - q_2 \equiv r$, $g_{12} = v_1 - v_2 \equiv g$; the subscripts (12) will be suppressed whenever there is no ambiguity]:

$$
\begin{aligned}
&\int dx_2 \int_0^t d\tau \, L'_{12} U^0_{12}(\tau) \, L'_{12} \, f(x_1; t - \tau) f(x_2; t - \tau) \\
&= \; m^{-2} \int dv_2 \, d\mathbf{r} \int_0^t d\tau \, \partial_{12} \cdot [\nabla_1 V(\mathbf{r})] \, [\nabla_1 V(\mathbf{r} - \mathbf{g}\tau)] \cdot \\
&\quad \times U^0_{12}(\tau) \, \partial_{12} \, U^0_{12}(-\tau) \, f(\mathbf{q}_1, \mathbf{v}_1; t) \, f(\mathbf{q}_1 - \mathbf{r}, \mathbf{v}_2; t) \, .
\end{aligned} \tag{6.15}
$$

We now note that the factor $V(\mathbf{r})$ differs from zero only when $r < l_C$; moreover, for given r, $V(\mathbf{r} - \mathbf{g}\tau)$ differs from zero only when $\tau < \tau_C$ [by the same argument as in Eq. (6.13)]. This means that *only the range of values $0 < r < l_C$ and $0 < \tau < \tau_C$ contributes effectively to the integrals in Eq. (6.15)*. It thus follows that, as we are interested in times $t \gg \tau_C$, the upper limit of the time integral can be extended from t to ∞ without appreciable error. With this in mind, we evaluate the following expression, taking care of the non-commutation of U^0 and ∂:

$$U^0_{12}(\tau) \, \partial_{12} U^0_{12}(-\tau) \, f(x_1; t) f(x_2; t) = (\partial_{12} + \tau \nabla_{12}) \, f(x_1; t) f(x_2; t) \, , \tag{6.16}$$

where $\nabla_{12} = \nabla_1 - \nabla_2$. [We used here Eq. (5.13) and the group property $U^0_{12}(\tau) \, U^0_{12}(-\tau) = 1$]. Next, we note [using Eqs. (6.7), (6.8)] that $\tau \nabla f f \approx V^{-1} (\tau_c / \tau_H) f f \approx$

$V^{-1}(\lambda^2\lambda_H) ff \ll \partial ff$ [here V is the typical thermal velocity]; the term $\tau\nabla_{12}$ is thus negligible. We also note:

$$f(\mathbf{q}_1 - \mathbf{r}) \approx (1 - \mathbf{r}\cdot\nabla_1) f(\mathbf{q}_1) \approx [1 - (l_c/l_H)] f(\mathbf{q}_1) \approx f(\mathbf{q}_1). \qquad (6.17)$$

This consequence of the length scale ordering (6.9) will be called the *local approximation*. After these operations, Eq. (6.15) reduces to:

$$\int dx_2 \int_0^t d\tau\, L'_{12} U^0_{12}(\tau)\, L'_{12}\, f(x_1; t-\tau) f(x_2; t-\tau)$$
$$= m^{-2} \int d\mathbf{v}_2 d\mathbf{r} \int_0^\infty d\tau\, \partial_{12}\cdot[\nabla_1 V(\mathbf{r})]\,[\nabla_1 V(\mathbf{r}-\mathbf{g}\tau)]\cdot\partial_{12}\, f(\mathbf{q}_1,\mathbf{v}_1; t)\, f(\mathbf{q}_1,\mathbf{v}_2; t)$$
$$\equiv \mathcal{K}\{f f\} \qquad (6.18)$$

In conclusion, the consistent application of the asymptotic treatment implied by the weak coupling hydrodynamic regime (6.7) - (6.10) leads to a considerable simplification of the master equation (6.4). Indeed, in the original form, the integrals over $\mathbf{r}$ and over τ involve both the interaction potential V and the unknown RDF's ff; the master equation is thus an *integro-differential* equation. In the asymptotic limit, the RDF's no longer depend on $\mathbf{r}$ or on τ and can be taken out of these integrals, which implies a serious simplification. This feature is particularly important for the time variable. The initial *non-Markovian* equation (6.15) [see Sec. 6.1] becomes asymptotically a purely differential *Markovian* equation. It describes a process in which the rate of change of the unknown $f(t)$ at any time only depends on the instantaneous state, and not of the previous history. The passage from (6.15) to (6.18) will be called a MARKOVIANIZATION PROCESS.

We now write the asymptotic equation of evolution by using Eqs. (6.4), (6.13), (6.18), and (5.21):

$$(\partial_t + \mathbf{v}_1\cdot\nabla_1)\, f(\mathbf{q}_1, \mathbf{v}_1; t) = \mathcal{V}\{f f\} + \mathcal{K}\{f f\}\,. \qquad (6.19)$$

This is the final form of the *kinetic equation for a weakly coupled system*, valid through order λ^2: it is called the LANDAU KINETIC EQUATION (or, sometimes, the Vlasov-Landau kinetic equation). The new term $\mathcal{K}\{f f\}$ is called the *Landau collision term*.

Before closing this section, we write down, for easy reference, the form of the kinetic equation for a *spatially homogeneous system*. In this case, the RDF has the form $f(\mathbf{q}, \mathbf{v}; t) = n\varphi(\mathbf{v}; t)$; the free motion term and the Vlasov term are identically zero [Eq. (5.24)], and the kinetic equation reduces to:

$$\partial_t\varphi(\mathbf{v}; t) = \mathcal{K}\{\varphi\varphi\}\,, \qquad (6.20)$$

with:[3]

$$\mathcal{K}\{\varphi\,\varphi\} = \frac{n}{m^2}\int d\mathbf{v}_2 d\mathbf{r}\int_0^{\infty} d\tau\,\partial_{12}\cdot\left[\nabla_1 V\left(\mathbf{r}\right)\right]\left[\nabla_1 V\left(\mathbf{r}-\mathbf{g}\tau\right)\right]\cdot\partial_{12}\,\varphi(\mathbf{v}_1;t)\varphi(\mathbf{v}_2;t)$$
(6.21)

We stress the obvious fact that the inhomogeneous collision term differs from the homogeneous one only by the replacement of the functions $n\varphi(\mathbf{v}_j;t)$ by the RDF's $f(\mathbf{q},\mathbf{v}_j;t)$, all evaluated at the same position.

6.3   Explicit form of the Landau collision term

The collision term (6.18) can be written in the form[4]:

$$\mathcal{K}\{f\,f\} = m^{-2}\int d\mathbf{v}_2\,\partial_{12}\cdot\mathbf{G}(\mathbf{g})\cdot\partial_{12}\,f(\mathbf{q}_1,\mathbf{v}_1;t)\,f(\mathbf{q}_1,\mathbf{v}_2;t)\,,$$
(6.22)

where $\mathbf{G}(\mathbf{g})$ is the *Landau tensor*, depending on the velocities $\mathbf{v}_1$, $\mathbf{v}_2$ only through their difference $\mathbf{g}=\mathbf{v}_1-\mathbf{v}_2$. This tensor is conveniently evaluated by using the Fourier representation of the interaction potential (2.30):

$$
\begin{aligned}
\mathbf{G}(\mathbf{g}) &= \int d\mathbf{r}\int_0^{\infty} d\tau\,\left[\nabla_1 V\left(\mathbf{r}\right)\right]\left[\nabla_1 V\left(\mathbf{r}-\mathbf{g}\tau\right)\right]\\
&= \int d\mathbf{r}\int_0^{\infty} d\tau\int d\mathbf{k}\,d\mathbf{k}'\,e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}-i\mathbf{k}'\cdot\mathbf{g}\tau}\left[i\mathbf{k}\widetilde{V}(\mathbf{k})\right]\left[i\mathbf{k}'\widetilde{V}(\mathbf{k}')\right]\\
&= (2\pi)^3\int d\mathbf{k}\int_0^{\infty} d\tau\,e^{i\mathbf{k}\cdot\mathbf{g}\tau}\left[i\mathbf{k}\widetilde{V}(\mathbf{k})\right]\left[-i\mathbf{k}\widetilde{V}(k)\right]\\
&= 8\pi^4\int d\mathbf{k}\,\delta_+(\mathbf{k}\cdot\mathbf{g})\left[i\mathbf{k}\widetilde{V}(k)\right]\left[-i\mathbf{k}\widetilde{V}(k)\right].
\end{aligned}
$$
(6.23)

We used here the following relation, defining the distribution (generalized function) $\delta_+(x)$:

$$\int_0^{\infty} dk\,e^{ikx} = \pi\delta_+(x) = \pi\delta(x) + i\mathcal{P}\left(\frac{1}{x}\right),$$
(6.24)

Given the importance of this distribution in statistical mechanics, we devote an Appendix to the discussion of the concepts related to it. Noting that the factor

---

[3]The collision term in the homogeneous case differs by a factor n from the inhomogeneous case (because of the relation $f=n\varphi$); the difference is not important enough to justify a different notation for the collision term $\mathcal{K}$ in the two cases.

[4]It may be useful to recall that here and in forthcoming formulae, a differential operator, such as ∂_{12}, acts on all functions written to its right. When we mean that a differential operator acts only on a specified function, we use parentheses, such as $[\nabla_1 V(r)]$ in Eq. (6.23).

multiplying $\delta_+(\mathbf{k} \cdot \mathbf{g})$ in (6.23) is an even function of $\mathbf{k}$, and that the principal part is odd, we find:

$$G(\mathbf{g}) = 8\pi^4 \int d\mathbf{k}\, \delta(\mathbf{k} \cdot \mathbf{g})\, \widetilde{V}^2(k)\, \mathbf{k}\, \mathbf{k}.$$

$$(6.25)$$

This is a first, useful form of the Landau tensor, yielding the following form for the collision term:

$$\mathcal{K}\{f\, f\} = \frac{8\pi^4}{m^2} \int d\mathbf{v}_2 \int d\mathbf{k}\, \widetilde{V}^2(k)\, (\mathbf{k} \cdot \partial_{12})\, \delta(\mathbf{k} \cdot \mathbf{g})\, (\mathbf{k} \cdot \partial_{12})\, f(\mathbf{q}_1, \mathbf{v}_1; t)\, f(\mathbf{q}_1, \mathbf{v}_2; t).$$

$$(6.26)$$

We can go further in the evaluation of the Landau tensor, by performing the integration over $\mathbf{k}$. We introduce a cartesian reference frame whose z-axis is parallel to the relative velocity $\mathbf{g}$, and use spherical coordinates (k, θ, ϕ) [Fig. 6.3]:
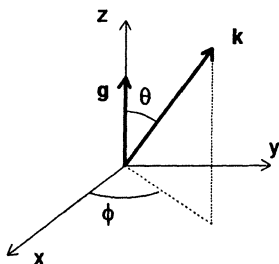
Figure 6.3: Reference frame for the evaluation of the collision term.

$$
\begin{aligned}
G(\mathbf{g}) \;=\; & 8\pi^4 \int_0^\infty dk \int_0^\pi d\theta \int_0^{2\pi} d\phi\, k^2 \sin\theta\, \widetilde{V}^2(k)\, \delta\left(kg\, \cos\theta\right) \\
& \times k^2 \left\{ \begin{array}{c} \sin\theta\, \cos\phi \\ \sin\theta\, \sin\phi \\ \cos\theta \end{array} \right\} \left\{ \begin{array}{c} \sin\theta\, \cos\phi \\ \sin\theta\, \sin\phi \\ \cos\theta \end{array} \right\}.
\end{aligned}
$$

$$(6.27)$$

By integration over ϕ we find that all non-diagonal components of this tensor are zero (in this reference frame); moreover, because of the δ-function, the zz-component also vanishes, and the xx- and yy-components are equal. The Landau tensor has the following form:

$$G = \begin{pmatrix} G & 0 & 0 \\ 0 & G & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

or,

$$G = (I - e_z\, e_z)\, G\,, \qquad (6.28)$$

where I is the unit tensor, and e_z is the unit vector along z. We now easily find:

$$G = 8\pi^5 \int_0^\infty dk\, \widetilde{V}^2(k)\, k^4 \int_0^\pi d\theta\, \sin\theta \sin^2\theta\, \delta\,(kg\,\cos\theta) = \frac{B}{g}\,, \qquad (6.29)$$

with:

$$B = 8\pi^5 \int_0^\infty dk\, \widetilde{V}^2(k)\, k^3\,. \qquad (6.30)$$

The tensor G can now be expressed in a form independent of the special reference frame chosen for its calculation by noting that $e_z = g/g$; its components are thus:

$$G_{rs} = \left(\delta_{rs} - \frac{g_r g_s}{g^2}\right)\frac{B}{g}\,, \qquad (6.31)$$

and the final form of the Landau collision term is:

$$\mathcal{K}\{f\,f\} = \frac{B}{m^2}\int dv_2\, \partial_1^r\, \frac{g^2\delta_{rs} - g_r g_s}{g^3}\, \partial_{12}^s\, f(\mathbf{q}_1,\mathbf{v}_1;t)\, f(\mathbf{q}_1,\mathbf{v}_2;t)\,. \qquad (6.32)$$

[Note that we replaced, without any error, the leftmost operator $\partial_{12}^r = \partial/\partial v_{1r} - \partial/\partial v_{2r}$ by ∂_1^r; see Eq. (4.26)].

Given the importance of the Landau equation in plasma physics, we also write it here explicitly for the two-species system (electrons + ions) considered in Sec. 5.3. [see (5.34)]:

$$\left[\partial_t + \mathbf{v}_1\cdot\nabla_1 + \frac{e_\alpha}{m_\alpha}\mathbf{E}\,(\mathbf{q}_1,t)\cdot\partial_1\right] f^\alpha(\mathbf{q}_1,\mathbf{v}_1;t) = \sum_{\beta=e,i}\mathcal{K}^{\alpha\beta}\{f\,f\}\,, \qquad (6.33)$$

with:

$$\begin{aligned}
\mathcal{K}^{\alpha\beta}\{f\,f\} &= B^{\alpha\beta}\int dv_2\frac{1}{m_\alpha}\frac{\partial}{\partial v_{1r}}\frac{g^2\delta_{rs} - g_r g_s}{g^3} \\
&\quad \times \left(\frac{1}{m_\alpha}\frac{\partial}{\partial v_{1s}} - \frac{1}{m_\beta}\frac{\partial}{\partial v_{1s}}\right) f^\alpha(\mathbf{q}_1,\mathbf{v}_1;t)\, f^\beta(\mathbf{q}_1,\mathbf{v}_2;t)\,. \qquad (6.34)
\end{aligned}$$

$B^{\alpha\beta}$ is the constant B of Eq. (6.30), evaluated with the Coulomb potential (or the Debye potential) of interaction between species α and β. At this step there appears a specific difficulty in the case of plasmas: it will be discussed in Chap. 8.

6.4   Conclusion

The Landau kinetic equation was derived from the Liouville equation, via the BBGKY hierarchy, by a systematic perturbation expansion. The following assumptions are formulated as explicitly as possible:

- A) *The thermodynamic limit;*

- B) *The weakness of the molecular interactions:* $\lambda \ll 1$;

- C) *The finite range of the interactions and of the correlations;*

- D) *A specific ordering of the length- and time-scales:* $l_C \ll l_{mfp} \ll l_H$; $\tau_C \ll \tau_R \ll \tau_H$;

- E) *An asymptotic treatment of the equations of evolution:* $t \gg \tau_C$.

The result of the implementation of the assumptions A) - E) is the appearance of a COLLISION TERM in the closed equation of evolution for the one-particle reduced distribution function (RDF) $f(\mathbf{q}, \mathbf{v}; t)$. Such an equation of evolution is called a KINETIC EQUATION.

The kinetic equation for a weakly coupled system is not the only one of its kind. By modifying assumption B), a whole class of kinetic equations can be derived, covering many different situations. Some of them will be considered in the next two chapters. We therefore postpone the discussion of their general properties, in order to exhibit the common features of widely different physical systems.

6.5   Appendix. The Cauchy Integral

We give here a very brief discussion of the properties of a mathematical object that appears very often in statistical dynamics. More extensive treatments will be found in the references quoted in BN6.

Let $f(x)$ be a sufficiently regular function of the *real* variable x, and let z be a *complex* variable. We define the CAUCHY INTEGRAL associated with $f(x)$ as follows:

$$\Phi(z) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \, \frac{f(x)}{x - z}. \tag{6.35}$$

The importance of this concept is due to the fact that the resolvent of the unperturbed Liouville equation is $[i\,(\mathbf{k}\cdot\mathbf{v}-z)]^{-1}$, as shown in Eq. (5.46). Hence, any perturbative theory will introduce such denominators, and thus Cauchy integrals.

$\Phi(z)$ is a regular (holomorphic) function of z in the whole upper half-plane (denoted by S_+) and also in the whole lower half-plane, S_-; it is, however, discontinuous along the whole real axis, because of the singularity of the integrand. The Cauchy integral actually tends toward different values as z approaches a point y the real axis from above or from below. To calculate these limiting values the contour of integration is slightly deformed by adjoining a semicircle of radius ε centered on the real limiting value y of z. The semicircle is oriented in such a way that z remains always on the same side of the contour as it tends to y [Fig. 6.4]; at the end of the calculation, ε tends to zero.
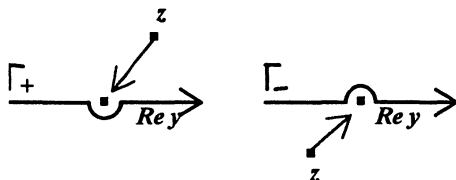
Figure 6.4: Contours of integration Γ_+ and Γ_-.

We introduce the definition of a *(Cauchy) principal part*:

$$\mathcal{P}\int_{-\infty}^{\infty} dx\,\frac{f(x)}{x-y} = \lim_{\varepsilon\to 0}\left\{\int_{-\infty}^{y-\varepsilon} dx\,\frac{f(x)}{x-y} + \int_{y+\varepsilon}^{\infty} dx\,\frac{f(x)}{x-y}\right\}, \quad \varepsilon > 0. \qquad (6.36)$$

The integral along the contour Γ_+ defining the limiting value $\Phi^{(+)}(y)$ of the Cauchy integral for $z \to y$ from above $(z \in S_+)$ is obtained as a sum of two terms: the principal value (6.36) and $\frac{1}{2}(2\pi i)$ times the residue of the integrand at $x = y$:

$$\Phi^{(+)}(y) = \frac{1}{2}f(y) + \frac{1}{2\pi i}\mathcal{P}\int_{-\infty}^{\infty} dx\,\frac{f(x)}{x-y}, \quad y : \text{real}. \qquad (6.37)$$

Similarly, one obtains the limiting value $\Phi^{(-)}(y)$ for $z \to y$ from below:

$$\Phi^{(-)}(y) = -\frac{1}{2}f(y) + \frac{1}{2\pi i}\mathcal{P}\int_{-\infty}^{\infty} dx\,\frac{f(x)}{x-y}, \quad y : \text{real}. \qquad (6.38)$$

These two equations are the central result of the theory of the Cauchy integral: they are called the *Plemelj formulae*. They clearly show that the function $\Phi(z)$ has a cut along the whole real axis, with a finite jump:

$$\Phi^{(+)}(y) - \Phi^{(-)}(y) = f(y), \quad y : \text{real}. \tag{6.39}$$

The Plemelj formulae can be rewritten by introducing two important distributions (generalized functions):

$$\delta_+(x) = \delta(x) + \frac{i}{\pi}\mathcal{P}\frac{1}{x},$$

$$\delta_-(x) = \delta(x) - \frac{i}{\pi}\mathcal{P}\frac{1}{x}. \tag{6.40}$$

Like all distributions, these only have a meaning in connection with an integration. These objects lead to an alternative, very interesting interpretation of the Plemelj formulae. These provide us with a decomposition of an arbitrary function $F(x)$ of a real variable x into a sum of two components, $F_+(x)$, $F_-(x)$ with the following properties: a *"plus-function"* [*"minus-function"*] has a regular analytic continuation into the upper [lower] half-plane S_+ [S_-]. The distributions $\delta_\pm(x)$ act as "projectors" onto these two subspaces:

$$F_+(y) = \frac{1}{2}\int_{-\infty}^{\infty} dx\,\delta_+(y-x)\,F(x), \quad y : \text{real}$$

$$F_-(y) = -\frac{1}{2}\int_{-\infty}^{\infty} dx\,\delta_-(y-x)\,F(x), \quad y : \text{real} \tag{6.41}$$

Clearly:

$$F_+(y) + F_-(y) = F(y). \tag{6.42}$$

Comparing these equations with the Plemelj formulae, we find the following important representation of the distributions $\delta_\pm(x)$:

$$\lim_{\varepsilon\to 0}\frac{1}{x+i\varepsilon} = -\pi i\,\delta_+(x),$$

$$\lim_{\varepsilon\to 0}\frac{1}{x-i\varepsilon} = \pi i\,\delta_-(x), \quad x : \text{real}, \quad \varepsilon > 0. \tag{6.43}$$

Another useful representation of these distributions (used in the main text) is easily obtained from (6.42):

$$\delta_+(x) = \frac{1}{\pi} \int_0^\infty dk\, e^{ikx},$$

$$\delta_-(x) = -\frac{1}{\pi} \int_0^\infty dk\, e^{-ikx}. \tag{6.44}$$

Before closing this appendix, we draw attention to the following unusual property: in an integral involving a product of two $\delta_\pm$ distributions, the order of integration cannot be changed freely. This is a consequence of a famous theorem due to Poincaré and Bertrand, which we quote without proof:

$$\int dx\, \frac{\mathcal{P}}{x-u} \int dy\, \frac{\mathcal{P}}{y-x} f(x,y)$$

$$= -\pi^2 f(u,u) + \int dy \int dx\, \frac{\mathcal{P}}{x-u} \frac{\mathcal{P}}{y-x} f(x,y). \tag{6.45}$$

6.6 Bibliographical Notes BN6

The Landau equation was first derived by a different method (from the Boltzmann equation):

Landau, L.D., 1936, Phys. Z. Sowj. Union, **10**, 154.

It was derived systematically by a perturbation theory by N.N. Bogolioubov, 1946 (**BN5**) and by R. Balescu, 1963 **RB-1** (**BN1**).

The Landau equation is discussed in all textbooks on plasma kinetic theory quoted in **BN5**. We may add, in particular:

Klimontovich, Yu.L., 1964, *The Statistical Theory of Nonequilibrium Processes in a Plasma*, Pergamon, Oxford,
Spohn, H., 1991 (**BN3**),
Balescu, R., 1988 **RB-3** (**BN1**).

The Cauchy Integral and related matters are discussed in great detail in:
Muskhelishvili, N.I., 1953, *Singular Integral Equations*, Noordhof, Groningen; see also:
Balescu, R., 1963, **RB-1** (**BN1**).

Chapter 7

Kinetic Equation for Dilute Gases

7.1   The Dilute Gas Ordering

After the derivation of the Landau kinetic equation for weakly coupled systems in Chap. 6, we now turn our attention to other types of systems. These are more realistic, but their treatment is accordingly more complicated. Actually, in most cases a complete analytical derivation of kinetic equations from the basic dynamical equations is not possible with the same amount of rigour as for weakly coupled systems. There are, however, two very important cases for which a true derivation of kinetic equations is possible: they are treated in the present and in the next chapter.

The main reason why the weak coupling model is unrealistic is the existence of a *hard core* in any type of molecular interaction; as a result, at sufficiently short distance, the repulsive force becomes arbitrarily strong. This point was discussed in Sec. 2.4 and illustrated in Figs. 2.1 and 2.2. If a realistic theory of systems with this type of interactions is desired, the strength of the interactions is not an appropriate expansion parameter. Another characteristic of the interaction potential can, however, be exploited. For all types of neutral molecules, this potential has a *finite range*, that was denoted as l_0 [see Eq. (5.8)]. For the Lennard-Jones potential (2.34) l_0 would be the position of the minimum, r_0; for the hard sphere potential (2.35) it is the diameter of the molecules. l_0 thus defines an intrinsic characteristic length depending only on the nature of the molecules. As follows from the discussion of Sec. 5.1, in many interesting cases, the length l_0 can also be identified with the correlation length l_C. On the other hand, there exists another characteristic length in the system: the *average distance* between the molecules, d. This length depends on the global state of the system, i.e., on the number density n. Within a numerical factor of order one, we have: $d = n^{-1/3}$. The ratio of the two lengths l_C/d [or, for convenience, $(l_C/d)^3$] defines a dimensionless *density parameter* that is independent of the interaction strength and is a good candidate for a perturbation expansion

different from the weak coupling expansion. This parameter will be small whenever the density n is sufficiently small: the theory will thus apply to very *dilute gases*. Specifically, we consider:

$$\gamma \equiv n l_C^3 \ll 1 . \tag{7.1}$$

We now formulate an alternative kinetic theory in which Assumption B) of Sec. 6.4 is replaced by (7.1), but Assumptions A), C), D), E) are kept unchanged. We stress the fact that no assumption is made about the interaction strength, which is now considered as a finite, possibly "large" quantity.

We first reconsider the ordering discussed in Sec. 5.1. The ordering with respect to γ will be determined by the density dependence. The Hamiltonian is clearly independent of the density, being an intrinsic property of the molecules; the same holds true for the Liouvillians, thus:

$$L_j^0 = O(\gamma^0), \quad L_{jn}' = O(\gamma^0) . \tag{7.2}$$

Consider now the reduced distribution function (RDF) and the correlation functions. Considering their physical meaning, it is clear that the RDF is proportional to the average density n [the form (4.20) is quite explicit in this respect], the two-particle correlation function is proportional to its square, and more generally:

$$f(x_1) = O(\gamma), \quad g_n(x_1, ..., x_n) = O(\gamma^n) . \tag{7.3}$$

Finally, we note that the interaction Liouvillian enters the equations of evolution of the correlations in two ways. In a "X-vertex", such as the first two vertices appearing in Fig. 4.5, L_{jn}' connects an initial and a final state with the same number of particles: it therefore introduces no additional density factor into the equation of evolution. In a "Y-vertex", such as those of Fig. 4.4, the interaction Liouvillian connects a p-particle state (at the left) to a $(p+1)$-particle state: it therefore introduces an additional factor n.

With this information, we possess all we need for the derivation of the kinetic equation.

7.2   The Boltzmann Equation

We consider a classical system of particles for which the condition (7.1) and the assumptions A), C), D), E) of Sec. 6.4 are satisfied. In a first stage, we consider a *spatially homogeneous system*, hence the RDF is of the form (4.20): $f(\mathbf{q}, \mathbf{v}; t) = n\varphi(\mathbf{v}; t)$. [Note that $\varphi(\mathbf{v}; t) = O(\gamma^0)$]. Its equation of evolution is obtained from Eq. (4.41), which for a homogeneous system reduces to:

$$\partial_t f(x_1; t) = \int d\mathbf{q}_2 d\mathbf{v}_2 \, L'_{12} \, g_2(x_1, x_2; t) . \tag{7.4}$$

There is no Vlasov term for a homogeneous system; but even for an inhomogeneous system, the Vlasov term is negligible under the assumptions C), D) [i.e., when $l_C \ll l_H$], as was shown in Sec. 5.3. Thus the only diagram representing the evolution of the RDF is the one shown in Fig. 7.1: this is a diagram of type Y. It therefore introduces a factor n in the evolution operator [indeed, the latter connects $n\varphi$ to g_2 which is $O(n^2)$]. The operator to leading order in γ will therefore be obtained by retaining g_2 to lowest order.
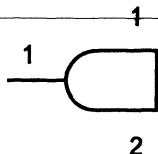
Figure 7.1: Diagram for the evolution of the RDF for a dilute gas.

Looking at Fig. 4.5 we see that the evolution to leading order will be given by the two diagrams involving an X-vertex; the others, involving a Y-vertex, contain an additional factor n. The relevant approximation to the equation of evolution thus corresponds to the diagrams of Fig. 7.2: here appears the difference with the weak coupling case (Fig. 6.1).
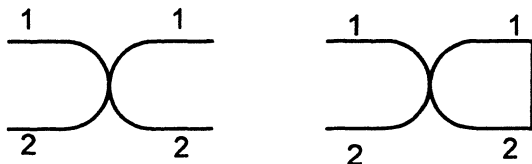
Figure 7.2: Diagrams for the evolution of the correlation function for a dilute gas.

The additional term introduces a new operator acting on g_2 but, as in the Landau case, there is no coupling to g_3:

$$\left(\partial_t - L_1^0 - L_2^0 - L'_{12} \right) g_2(x_1, x_2; t) = L'_{12} \, f(x_1; t) f(x_2; t) . \tag{7.5}$$

This equation has a clear and simple physical meaning: it is an inhomogeneous Liouville equation with a source term. As in the Landau case, the latter is quite important, because it allows the correlation function to be expressed as a functional of $f(x_1; t)$. The left hand side is the Liouville equation for a *complete two-body problem, including the interactions*. Here lies the main difference with the Landau case, where only the unperturbed two-body Liouvillian was retained in Eq. (6.2), as a result of the weak coupling approximation. Here, the interactions are treated on the same footing as the free motion. We therefore have to solve the classical *two-body problem*. This is an integrable problem, as we know from classical mechanics. Finally, we note that the absence of three-body correlations means that we will obtain a kinetic equation involving only binary collisions (like the Landau equation). Indeed, in a dilute gas, three-body collisions are extremely rare.

On the basis of these remarks, the first steps of the derivation will be closely analogous to those of Secs. 6.1 and 6.2. The difference is that instead of the unperturbed propagator $U_{12}^0(t)$, we must use the *complete two-body propagator* $Y_{12}(t)$ for the solution of the correlation equation (7.5); the latter is defined as the solution of the following initial value problem:

$$\partial_t Y_{12}(t) - \left(L_1^0 + L_2^0 + L_{12}' \right) Y_{12}(t) = 0, \quad Y_{12}(0) = I \,, \tag{7.6}$$

where I is the identity operator. We thus solve Eq. (7.5) as in (6.3) and substitute the result into (7.4), thus obtaining a non-Markovian master equation analogous to (6.4) (for a homogeneous system):

$$
\begin{aligned}
\partial_t \varphi(\mathbf{v}_1; t) &= n \int_0^t d\tau \int d\mathbf{q}_2 d\mathbf{v}_2 \, L_{12}' Y_{12}(\tau) L_{12}' \, \varphi(\mathbf{v}_1; t - \tau)\varphi(\mathbf{v}_2; t - \tau) \\
&\quad + n^{-1} \int d\mathbf{q}_2 d\mathbf{v}_2 \, L_{12}' Y_{12}(t) \, g_2(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; 0) \,.
\end{aligned} \tag{7.7}
$$

The assumptions C), D), E) of Sec. 6.4. are still applicable and allow us to proceed with an asymptotic treatment that leads to a Markovian equation of evolution, which we write in the following form:

$$\partial_t \varphi(\mathbf{v}_1; t) = n \int d\mathbf{v}_2 \, J(\mathbf{v}_1, \mathbf{v}_2) \tag{7.8}$$

with:

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int d\mathbf{r} \int_0^\infty d\tau \, L_{12}' Y_{12}(\tau) L_{12}' \, \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) \,. \tag{7.9}$$

In order to evaluate this expression we need to study the propagator $Y_{12}(\tau)$. We first simplify the notations. We go over to centre-of-mass coordinates and relative coordinates, both for the positions and for the velocities:

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{q}_1 + \mathbf{q}_2), \quad \mathbf{r} = \mathbf{q}_1 - \mathbf{q}_2,$$
$$\mathbf{G} = \tfrac{1}{2}(\mathbf{v}_1 + \mathbf{v}_2), \quad \mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2. \tag{7.10}$$

In terms of these variables, the Liouvillians become:

$$L_1^0 + L_2^0 = -\mathbf{G} \cdot \nabla_R - \mathbf{g} \cdot \nabla, \qquad L_{12}' = \frac{2}{m}\left[\nabla V(r)\right] \cdot \partial. \tag{7.11}$$

where we use now: $\nabla_R = \partial/\partial\mathbf{R}$, $\nabla = \partial/\partial\mathbf{r}$, $\partial = \partial/\partial\mathbf{g}$. In a homogeneous system all functions depend on positions only through the relative distance $\mathbf{r}$, hence the term $\mathbf{G} \cdot \nabla_R$ is effectively zero.

We now go back to Eq. (7.6), which we rewrite as:

$$\partial_t Y_{12}(t) - \left(L_1^0 + L_2^0\right) Y_{12}(t) = L_{12}' Y_{12}(t) \tag{7.12}$$

If we consider formally the right hand side as a source term, this equation has the same form as an inhomogeneous unperturbed Liouville equation, and is solved in terms of the unperturbed propagator $U_{12}^0(t)$ (5.17):

$$Y(t) = U^0(t) + \int_0^t d\tau\, U^0(t - \tau) L' Y(\tau). \tag{7.13}$$

(From here on we suppress the superfluous subscripts 12) Using Eqs. (7.11), (5.17) and (5.13), the unperturbed two-body propagator reduces, for a homogeneous system, to:

$$U^0(t) = \exp(-\mathbf{g}\, t \cdot \nabla). \tag{7.14}$$

We thus transformed Eq. (7.12) into an integral equation. Note that only the integral of $Y(t)$ over time enters the kinetic equation (7.9). We thus integrate both sides of (7.13) over t from 0 to ∞, and introduce new, time-independent operators:[1]

$$G = \int_0^\infty dt\, U^0(t), \qquad Z = \int_0^\infty dt\, Y(t), \tag{7.15}$$

we find (after an obvious change of integration variables) the following integral equation generated by (7.13):

$$Z = G + G\, L'\, Z. \tag{7.16}$$

---

[1]The definition of G poses a problem of convergence. Strictly speaking, $U^0(t)$ should be multiplied by a convergence factor $\exp(-\epsilon t)$, and the limit $\epsilon \to 0$ should be taken at the end of the calculation. We do not insist on this technical point here.

The action of the operator G on an arbitrary function $h(\mathbf{r}, \mathbf{g})$ is expressed as follows [using Eq. (5.14)]:

$$
\begin{aligned}
G\, h(\mathbf{r}, \mathbf{g}) &= \int_0^\infty dt \, \exp\left(-t\mathbf{g} \cdot \nabla\right) h(\mathbf{r}, \mathbf{g}) = \int_0^\infty dt \, h(\mathbf{r} - \mathbf{g}t, \mathbf{g}) \\
&= \int_0^\infty dt \int d\mathbf{r}' d\mathbf{g}' \, \delta\left(\mathbf{r} - \mathbf{g}t - \mathbf{r}'\right) \delta\left(\mathbf{g} - \mathbf{g}'\right) h(\mathbf{r}', \mathbf{g}') \\
&= \int d\mathbf{r}' d\mathbf{g}' \, G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) \, \delta\left(\mathbf{g} - \mathbf{g}'\right) h(\mathbf{r}', \mathbf{g}') \qquad (7.17)
\end{aligned}
$$

with:

$$
G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) = \int_0^\infty dt \, \delta\left(\mathbf{r} - \mathbf{g}t - \mathbf{r}'\right). \qquad (7.18)
$$

We now write Eq. (7.16) in terms of matrix elements. Noting that (7.17) implies:

$$
G\left(\mathbf{r}, \mathbf{g} \,|\, \mathbf{r}', \mathbf{g}'\right) = G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) \, \delta\left(\mathbf{g} - \mathbf{g}'\right), \qquad (7.19)
$$

we find:

$$
\begin{aligned}
Z\left(\mathbf{r}, \mathbf{g} \,|\, \mathbf{r}', \mathbf{g}'\right) &= G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) \, \delta\left(\mathbf{g} - \mathbf{g}'\right) \\
&+ \int d\mathbf{r}'' d\mathbf{g}'' G^0(\mathbf{r} - \mathbf{r}''; \mathbf{g}) \, \delta\left(\mathbf{g} - \mathbf{g}''\right) \tfrac{2}{m} \left[\nabla'' V(r'')\right] \cdot \partial'' Z\left(\mathbf{r}'', \mathbf{g}'' \,|\, \mathbf{r}', \mathbf{g}'\right) \quad (7.20)
\end{aligned}
$$

We now show that $G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g})$ has a simple physical meaning. Consider the following relation [otained by using Eqs. (6.40), (6.44)]:

$$
\begin{aligned}
\left(L_1^0 + L_2^0\right) G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) &= \mathbf{g} \cdot \nabla \int_0^\infty dt \, \delta\left(\mathbf{r} - \mathbf{g}t - \mathbf{r}'\right) \\
&= (2\pi)^{-3} \int_0^\infty dt \int d\mathbf{k} \, i\mathbf{k} \cdot \mathbf{g} \, \exp\left[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{g}t - \mathbf{r}')\right] \\
&= (2\pi)^{-3} \int d\mathbf{k} \, \exp\left[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')\right] i\mathbf{k} \cdot \mathbf{g} \, \pi\delta_-\left(\mathbf{k} \cdot \mathbf{g}\right) \\
&= (2\pi)^{-3} \int d\mathbf{k} \, \exp\left[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')\right] \\
&= \delta\left(\mathbf{r} - \mathbf{r}'\right)
\end{aligned}
$$

[We used here the following identity: $ix\,\pi\delta_-(x) = ix\left[\pi\delta(x) + i^{-1}\mathcal{P}(1/x)\right] = 1$]. Thus:

$$
\mathbf{g} \cdot \nabla G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) = \delta\left(\mathbf{r} - \mathbf{r}'\right). \qquad (7.21)
$$

This means that $G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g})$ is the *Green's function* associated with the *unperturbed stationary* two-body Liouville equation $\mathbf{g} \cdot \nabla f(\mathbf{r}) = 0$. Note that $\mathbf{g}$ is here a mere parameter. Combining Eqs. (7.20) and (7.21) we find that Z is the *Green's function for the complete stationary two-body problem (including the interactions)*:

$$\left\{ \mathbf{g} \cdot \nabla - \frac{2}{m} \left[\nabla V(r) \right] \cdot \partial \right\} Z \left(\mathbf{r}, \mathbf{g} \,|\, \mathbf{r}', \mathbf{g}' \right) = \delta \left(\mathbf{r} - \mathbf{r}' \right) \delta \left(\mathbf{g} - \mathbf{g}' \right). \tag{7.22}$$

Consider the function $f(\mathbf{r}; \mathbf{g}, \mathbf{G}, t) \equiv f(\mathbf{r}; \mathbf{g}, \mathbf{G})$ defined as follows[2]:

$$f(\mathbf{r}; \mathbf{g}, \mathbf{G}) = \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)$$
$$+ \int d\mathbf{r}' d\mathbf{g}' \, Z \left(\mathbf{r}, \mathbf{g} \,|\, \mathbf{r}', \mathbf{g}' \right) \tfrac{2}{m} \left[\nabla' V(r') \right] \cdot \partial' \, \varphi(\mathbf{v}_1'; t)\varphi(\mathbf{v}_2'; t) . \tag{7.23}$$

From the Green's function property of Z follows that $f(\mathbf{r}; \mathbf{g}, \mathbf{G})$ is a *stationary solution of the two-body Liouville equation*:

$$\left\{ \mathbf{g} \cdot \nabla - \tfrac{2}{m} \left[\nabla V(r) \right] \cdot \partial \right\} f(\mathbf{r}; \mathbf{g}; \mathbf{G}) = 0 , \tag{7.24}$$

with the limiting condition:

$$\lim_{V \to 0} f(\mathbf{r}; \mathbf{g}, \mathbf{G}) = \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) . \tag{7.25}$$

These equations are equivalent to the integral equation:

$$f(\mathbf{r}; \mathbf{g}, \mathbf{G}) = \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) + \int d\mathbf{r}' \, G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) \tfrac{2}{m} \left[\nabla' V(r') \right] \cdot \partial' f(\mathbf{r}'; \mathbf{g}, \mathbf{G}) . \tag{7.26}$$

At this point we can make a clear connection with scattering theory. Consider an incident beam of particles, described by the homogeneous distribution $\varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)$. As the beam passes the potential center (in the center-of-mass reference frame), its particles are scattered and, after a sufficient time ($t \approx \tau_C$), a new stationary distribution sets in. This distribution, which is a superposition of the incoming "wave" and of the scattered "wave" is described by the function $f(\mathbf{r}; \mathbf{g}, \mathbf{G})$.

Combining now Eqs. (7.9), (7.15) and (7.26) we find that the collision term in the kinetic equation can be written as:

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int d\mathbf{r} \tfrac{2}{m} \left[\nabla V(r) \right] \cdot \partial \left\{ f(\mathbf{r}; \mathbf{g}, \mathbf{G}) - \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) \right\} .$$

---

[2]For brevity, we do not write explicitly the variable t. In the right hand side of (7.23) and in forthcoming equations, it is understood that the variables $\mathbf{v}_1$, $\mathbf{v}_2$ are expressed in terms of $\mathbf{g}$, $\mathbf{G}$ through Eq. (7.10).

Note that the distance-independent function $\varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)$ does not contribute to the integral [as a result of (4.26)]; hence, using (7.24):

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int d\mathbf{r}\,\mathbf{g} \cdot \nabla f(\mathbf{r}; \mathbf{g}, \mathbf{G}) \qquad (7.27)$$

The function $G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g})$ has a very simple form in a reference frame where the z-axis is parallel to $\mathbf{g}$:

$$G^0(\mathbf{r} - \mathbf{r}'; \mathbf{g}) = g^{-1}\delta(x - x')\delta(y - y')\,\Theta(z - z') \qquad (7.28)$$

where $\Theta(x)$ is Heaviside's step function:

$$\Theta(x) = \begin{cases} 0, & for\ x < 0 \\ 1, & for\ x > 0 \end{cases} \qquad (7.29)$$

[It is immediately checked that (7.28) satisfies Eq. (7.21)]. Substituting this form into (7.26) and using (7.24) we find:

$$
\begin{aligned}
f(x, y, z; \mathbf{g}, \mathbf{G}) &= \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) + \int_{-\infty}^{z} dz'\, g^{-1}\tfrac{2}{m}\left[\nabla'V(x, y, z')\right] \cdot \partial f(x, y, z'; \mathbf{g}, \mathbf{G}) \\
&= \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t) + \int_{-\infty}^{z} dz'\, \frac{\partial}{\partial z'}\, f(x, y, z'; \mathbf{g}, \mathbf{G})\,. \qquad (7.30)
\end{aligned}
$$

This result is now substituted into the collision term (7.27):

$$
\begin{aligned}
J(\mathbf{v}_1, \mathbf{v}_2) &= \int dx\,dy \int_{-\infty}^{\infty} dz\, g\frac{\partial}{\partial z}\, f(x, y, z; \mathbf{g}, \mathbf{G}) \\
&= \int dx\,dy\, g\, [f(x, y, \infty; \mathbf{g}, \mathbf{G}) - f(x, y, -\infty; \mathbf{g}, \mathbf{G})] \qquad (7.31)
\end{aligned}
$$

From Eq. (7.30) we see that $f(x, y, -\infty; \mathbf{g}, \mathbf{G})$, i.e., the distribution of the incoming flux, is simply:

$$f(x, y, -\infty; \mathbf{g}, \mathbf{G}) = \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)\,. \qquad (7.32)$$

The function $f(x, y, +\infty; \mathbf{g}, \mathbf{G})$ represents the distribution of outgoing particles with relative velocity $\mathbf{g}$, far from the scattering center, i.e., far from the region of effective interaction. These particles result from a collision of incoming particles having velocities $\mathbf{v}_1'$, $\mathbf{v}_2'$, such that their velocities after the collision be exactly $\mathbf{v}_1$, $\mathbf{v}_2$. The value of these velocities is determined by the solution of the two-body problem [this problem is dealt with in the next section]: they are functions of the velocities $\mathbf{v}_1$, $\mathbf{v}_2$: $\mathbf{v}_i' = \mathbf{v}_i'(\mathbf{v}_1, \mathbf{v}_2)$. As we are dealing here with a closed two-body problem, we may use the Liouville theorem. It tells us that the distribution of the outgoing particles

at the point $(\mathbf{v}_1, \mathbf{v}_2)$ in velocity space is the same as the distribution of incoming particles [i.e. (7.32)] evaluated at a point traced back to $z \to -\infty$ along their orbit, i.e., the point $(\mathbf{v}_1', \mathbf{v}_2')$:

$$f(x, y, +\infty; \mathbf{g}, \mathbf{G}) = \varphi(\mathbf{v}_1'; t)\varphi(\mathbf{v}_2'; t) \,. \tag{7.33}$$

Calling b the radial coordinate in our cylindrical coordinate system, and ϕ the azimuthal angle, we combine Eqs. (7.8) and (7.31) - (7.33) and obtain the final form of the equation of evolution of the RDF:

$$\partial_t \varphi(\mathbf{v}_1; t) = n \int d\mathbf{v}_2 \int_0^{2\pi} d\phi \int_0^\infty db\, bg\, [\varphi(\mathbf{v}_1'; t)\varphi(\mathbf{v}_2'; t) - \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)] \,. \tag{7.34}$$

This is the celebrated BOLTZMANN KINETIC EQUATION *for dilute gases*, derived by *L. Boltzmann* in 1872. It was the first kinetic equation ever obtained in history, hence, it was the starting point of statistical dynamics. Boltzmann obtained his equation by using simple semi-intuitive arguments (see Sec. 9.3). The treatment presented here is much more involved than the original one; it is, however, a "true" derivation of the kinetic equation from first principles (the BBGKY hierarchy) under explicitly stated assumptions.

7.3   Implementation of the Boltzmann Equation

The implementation of the Boltzmann equation requires the explicit solution of the two-body problem. The form of the interaction potential is actually hidden in the deceptively simple form of Eq. (7.34): the form of the functions $\mathbf{v}_i' = \mathbf{v}_i'(\mathbf{v}_1, \mathbf{v}_2)$ depends, of course, crucially on the latter. We now briefly review the two-body problem.

Consider two point particles of equal mass m that undergo a collision. Let their velocities in the distant past before the collision be $(\mathbf{v}_1, \mathbf{v}_2)$ and their velocities in the distant future after the collision be $(\mathbf{v}_1', \mathbf{v}_2')$. The laws of conservation of momentum and of energy[3] provide us with four equations:

$$\begin{aligned} \mathbf{v}_1 + \mathbf{v}_2 &= \mathbf{v}_1' + \mathbf{v}_2' \,, \\ v_1^2 + v_2^2 &= v_1'^2 + v_2'^2 \,. \end{aligned} \tag{7.35}$$

---

[3]In an elastic collision the kinetic energy is conserved; point particles can only undergo elastic collisions. For composite particles the initial kinetic energy can be transformed partially into energy of the internal degrees of freedom (vibration, rotation,...) upon an inelastic collision.

Clearly, these equations are insufficient for the determination of the six components of $(\mathbf{v}'_1, \mathbf{v}'_2)$: two degrees of freedom remain undetermined. More definitely, calling $\mathbf{g}$ the relative velocity before the collision:

$$\mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2 , \tag{7.36}$$

we find:

$$
\begin{aligned}
\mathbf{v}'_1 &= \tfrac{1}{2}\left(\mathbf{v}_1 + \mathbf{v}_2 + g\mathbf{e}\right) , \\
\mathbf{v}'_1 &= \tfrac{1}{2}\left(\mathbf{v}_1 + \mathbf{v}_2 - g\mathbf{e}\right) ,
\end{aligned}
\tag{7.37}
$$

where e is a unit vector in an *arbitrary* direction (this reflects the indetermination mentioned above). It is also seen that the effect of the collision is a rotation of the vector $\mathbf{g}$, without change of its magnitude:

$$\mathbf{g}' = \mathbf{v}'_1 - \mathbf{v}'_2 = g\mathbf{e} . \tag{7.38}$$

In order to completely determine the solution, the parameters of the collision must be more closely defined. It is known that, because of the Galilei invariance, the two-body problem can always be reduced to two uncoupled one-body problems: the centre-of-mass motion, that is a trivial linear motion with velocity $\tfrac{1}{2}\left(\mathbf{v}_1 + \mathbf{v}_2\right)$ (a constant of the motion), and a motion relative to the centre-of-mass. The geometry is described in Fig. 7.3. The instantaneous position of the particle is described by polar coordinates r, θ in the plane of the trajectory. r_m, θ_m are the coordinates of the point of closest approach A to the centre of mass O. In absence of interaction, the distance of closest approach would be b, the *impact parameter*: an important quantity in the problem. [Note that b is the same quantity that appeared in Eq. (7.34)]. b could also be defined as the distance of the centre of mass to any of the two asymptotes of the trajectory. The angle χ between initial and final relative velocity vectors is called the *angle of deflection*. Thus, the unit vector e has components $(\sin\chi, \cos\chi)$ in the plane of the orbit.

For any central potential $V(r)$, the angle χ is entirely determined by the impact parameter b. χ is related to the angular coordinate of the point of closest approach as follows:

$$\chi = \pi - 2\theta_m . \tag{7.39}$$

The classical solution of the two-body problem (which we do not expose here) yields the following expression:

$$\theta_m = \int_{r_m}^{\infty} \frac{b/r^2}{\left\{1 - (b/r)^2 - [4V(r)/mg^2]\right\}^{1/2}} . \tag{7.40}$$
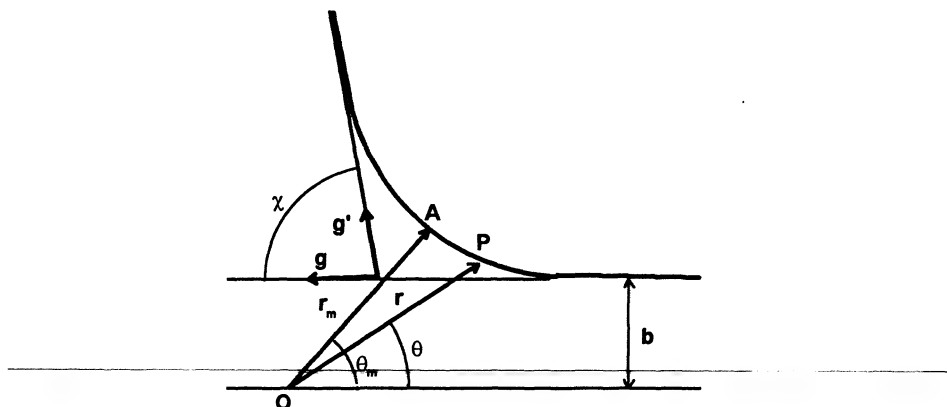
Figure 7.3: Geometry of a two-body collision

Eqs. (7.37) - (7.40) provide us with the complete solution of the mechanical problem: the velocities $\mathbf{v}'_1$, $\mathbf{v}'_2$ are completely determined in terms of the initial relative velocity $\mathbf{g}$ and the impact parameter b, for a given interaction potential $V(r)$. All the elements of Eq. (7.34) are thus determined in terms of the integration variables b and $\mathbf{g}$ (hence $\mathbf{v}_2$). Clearly, the solution is far from simple, and the explicit analytical calculations can only be done for a few specific models of interactions.

We now go back to Eq. (7.34) and rewrite it in a slightly different form. Let F denote the incident flux of particles, that is, the number of particles crossing, per unit time, a unit area element perpendicular to $\mathbf{g}$. It can easily be shown that the number of particles scattered per unit time into the solid angle defined by the cones of aperture χ and $\chi + d\chi$ is:

$$dN = F \, 2\pi b \, db. \tag{7.41}$$

Indeed, all incident particles contained in a cylindrical shell $(b, b + db)$ around the Ox axis, whose area is $2\pi b \, db$, will be scattered into the cone mentioned above, because χ is completely determined by b. The ratio dN/F is a well-known quantity in scattering theory: it is called the *differential cross-section* $d\sigma$ for the collision process under consideration. The differential cross-section can be expressed in terms of the angle of deflection χ. If the potential $V(r)$ is such that the angle of deflection is expressed by (7.40) as a monotonously decreasing function of b (which is physically

reasonable, at least for a repulsive potential), the latter equation can be reverted, expressing b in terms of χ. We then write:

$$d\sigma = b(\chi) \left| \frac{db(\chi)}{d\chi} \right| 2\pi d\chi$$

Noting also that the solid angle element defined above is $d\Omega = 2\pi \sin \chi \, d\chi$, we write the differential cross-section as:

$$d\sigma = \sigma \, d\Omega \,, \tag{7.42}$$

with:

$$\sigma = \frac{b(\chi)}{\sin \chi} \left| \frac{db(\chi)}{d\chi} \right| . \tag{7.43}$$

The Boltzmann equation is then written in the form:

$$\partial_t \varphi(\mathbf{v}_1; t) = n \int d\mathbf{v}_2 \int d\Omega \, g\sigma \, [\varphi(\mathbf{v}_1'; t)\varphi(\mathbf{v}_2'; t) - \varphi(\mathbf{v}_1; t)\varphi(\mathbf{v}_2; t)] \,. \tag{7.44}$$

The scattering cross-section cannot, in general, be calculated analytically except for a few models. The simplest of these (though physically not very realistic) is the *hard sphere model* (2.35). In that case the integral (7.40) is easily calculated, and one obtains:

$$b = r_0 \cos(\chi/2) \,, \tag{7.45}$$

and the cross-section:

$$\sigma = \tfrac{1}{4} r_0^2 \,. \tag{7.46}$$

This result, independent of both χ and g, is of course particularly simple and is widely used for explicit approximate calculations.

The kinetic equation for a *spatially inhomogeneous dilute gas* is obtained by a generalization of the calculation of Sec. 6.2, which we do not expose in detail. The result is easily understood. Whenever the assumptions C) - E) of Sec. 6.4 are valid, the kinetic equation has the form (6.19) (without the Vlasov term, which is small for short range forces, see Fig. 5.2):

$$\partial_t f(\mathbf{q}, \mathbf{v}; t) = -\mathbf{v} \cdot \nabla f(\mathbf{q}, \mathbf{v}; t) + \mathcal{K}^B \{f\,f\} \,, \tag{7.47}$$

with:

$$\mathcal{K}^B \{f\,f\} = \int d\mathbf{v}_1 \int_0^{2\pi} d\phi \int_0^{\infty} db\,bg \left[f(\mathbf{q}, \mathbf{v}'; t)\,f(\mathbf{q}, \mathbf{v}'_1; t) - f(\mathbf{q}, \mathbf{v}; t)\,f(\mathbf{q}, \mathbf{v}_1; t) \right].$$
$$(7.48)$$

Thus, the collision term has the same form as in a homogeneous system, but acts on inhomogeneous RDF's. The important point is that the collision appears as a *localized process*: the distribution functions are evaluated at the same point $\mathbf{q}$: this is a consequence of assumption C) of Sec. 6.4; its consequences will be discussed in Chap. 9.

7.4   Bibliographical Notes BN7

The Boltzmann Equation first appeared in:

Boltzmann, L., 1872, Wien. Berichte, **66**, 275;   see also:

Boltzmann, L., 1896, *Vorlesungen über Gastheorie*, Leipzig [Engl. transl.: *Lectures on gas theory*, S. Brush, transl., Univ. Calif. Press, Berkeley, 1964].

The first modern derivations of the Boltzmann equation from the Liouville (or the BBGKY) equation were given in:

Bogolioubov, N.N., 1946 (**BN5**),

Brout, R., 1956, Physica, **22**, 509,

Résibois, P., 1967, in: *Many-Particle Physics*, (E. Meeron, ed.), Gordon and Breach, New York,

Balescu, R., 1975 (**RB-2, BN1**).

A classical reference treating the Boltzmann equation and its solutions is:

Chapman, S. and Cowling, T.G., 1952, *The Mathematical Theory of Non-uniform Gases*, (2-nd ed.), Cambridge Univ. Press.

Among the numerous works devoted to this equation and some of its extensions, we quote the following ones:

Hirschfelder, J.O., Curtiss, C.F. and Bird, R.B., 1954, *Molecular Theory of Gases and Liquids*, Wiley, New York,

Uhlenbeck, G.E. and Ford, G., 1963, *Lectures in Statistical Mechanics*, Amer. Math. Soc., Providence,

Kogan, M.N., 1969, *Rarefied Gas Dynamics*, Plenum, New York,

Résibois, P. and De Leener, M., 1977, *Classical Kinetic Theory of Fluids*, Wiley, New York,

Ernst, M.H., 1980, "Exact solutions of the Boltzmann Equation", in: *Fundamental Problems in Statistical Mechanics, V*, (E.G.D. Cohen, ed.), North Holland, Amsterdam,

Cohen, E.G.D., 1980, "The Boltzmann Equation and Fluctuations", ibid.,

Montroll, E.W. and Lebowitz, J.L., 1983, *Studies in Statistical Mechanics,* vol. X, *Nonequilibrium phenomena I, The Boltzmann Equation,* North Holland, Amsterdam,

Cercignani, C., (ed.), 1984, *Kinetic Theories and the Boltzmann Equation,* Springer, Berlin,

Cercignani, C., 1988, *The Boltzmann Equation and its Applications,* Springer, Berlin.

Rigorous mathematical derivations and discussions of the Boltzmann equation are found in:

Grad, H., 1958, in: *Handbuch der Physik,* Band 12, Springer, Berlin,

Lanford, O.E., 1975, in: Proc. 1974 Batelle Rencontre on Dynamical Systems, (J. Moser, ed.), Springer, Berlin,

Lanford, O.E., 1983, "On a derivation of the BE", in: Montroll, E.W. and Lebowitz, J.L. (see above), p. 1,

Lasota, A. and Mackey, M.C., 1985, *Probabilistic Properties of Deterministic Systems,* Cambridge Univ. Press, Cambridge,

Spohn, H., 1991 (**BN3**).

Extensions of the Boltzmann Equation have been attempted in a variety of directions. Remaining in the domain of dilute gases, the theory of *polyatomic molecules* was developed. In dealing with internal degrees of freedom, such as rotation, vibration, spin, a quantum mechanical theory is indispensable. This type of theories is very important for comparison with experiment. The basic equation in this respect is the *Waldmann-Snider equation,* derived in:

Waldmann, L., 1957, Z. Naturforsch., **12A**, 660,

Snider, R.F., 1960, J. Chem. Phys., **32**, 1051;   a comprehensive review is:

Moraal, H., 1975, Phys. Reports, **17**, 225.

These matters are developed in great detail in a recent book:

McCourt, F.R.W., Beenakker, J.J.M., Kohler, W.E. and Kuščer, I., 1991, *Nonequilibrium Phenomena in Polyatomic Gases,* 2 vols., Clarendon Press, Oxford.

The extension toward *moderately dense gases* was attempted very early in a classical work:

Enskog, D., 1921, Kungl. Svenska Vet. Akad. Handl., **63**, No. 4.

Detailed discussions of the Enskog equation are found in: Chapman and Cowling, 1952, Hirschfelder et al., 1954, Résibois and De Leener, 1977 (quoted above).

The Enskog equation, derived for hard spheres, mainly takes into account the finite size of the latter [instead of evaluating the RDF's of the collision partners at the same point, one finds products of the form $f(\mathbf{q}, \mathbf{v}'; t) f(\mathbf{q}+d_0\varepsilon, \mathbf{v}'_1; t)$ in the collision term,

where d_0 is the diameter of the hard spheres and ε a unit vetor along the line of centers.

A systematic attack from a dynamical theory was done by:

Choh, S.T. and Uhlenbeck, 1958, *The Kinetic Theory of Dense Gases*, Univ. Michigan Report,

Cohen, E.G.D., 1956, Physica, **28**, 1025, 1045, 1060;

Résibois, P., 1964, Phys. Lett., **9**, 139.

In these works a first correction, proportional to the density, was obtained for the transport coefficients. Scientists in the field tried to derive a systematic expansion in powers of n (virial expansion): this proved to be an unexpected failure: the four-body collision term (three-body collisions already in 2 dimensions) is divergent!

Weinstock, J., 1963, Phys. Rev., **132**, 454,

Dorfman, J.R. and Cohen, E.G.D., 1965, Phys. Lett., **16**, 124; 1964, J. Math. Phys., **8**, 282.

This means that the transport coefficients are not analytic functions of n (why should they be?). A rearrangement of the terms (partial infinite summations of diagrams) leads to expressions (e.g. for the thermal conductivityof the following form (in 3 dimensions): $\kappa = \kappa^{(0)} + \kappa^{(1)} n + \kappa^{(a)} n^2 \ln n + \kappa^{(2)} n^2 + ..$ It turns out, however, that the logarithmic terms are very small compared to the analytic ones; thus a "virial expansion" may be a good approximation after all!

Kawasaki, K. and Oppenheim, I., 1965, Phys. Rev., **139**, A1763,

Weinstock, J., 1965, Phys. Rev., **140**, A460,

Sengers, J.V., 1966, Phys. Fluids, **9**, 1333, 1685, see also:

McLennan, J.A., 1989 (**BN3**).

Chapter 8

Kinetic Equation for Plasmas

8.1 The Plasma Ordering

We consider here a problem that was left open in the matters treated in Chaps. 6 and 7. An important class of systems, i.e., *plasmas* consisting of charged particles, does not seem to conform to all the assumptions listed in Sec. 6.4 that appeared to be necessary for the derivation of a kinetic equation. In particular, Assumption C) requiring a *finite range of the interaction potential* is violated by the Coulomb interactions. The long range of these interactions produces an important Vlasov average potential that adequately describes the collective behaviour of these systems, as shown in Chap. 5. The Vlasov equation is not sufficient, however, for explaining the irreversible evolution to equilibrium that is observed in plasmas as in any other macroscopic system. In the Vlasov picture the particles are "smeared out", there is nothing resembling a localized collision process. An important question thus arises: *How can we describe collisions in a plasma, and what is the mechanism of evolution in such a system with long range interactions?*

The difficulty introduced by the Coulomb interaction can be understood as follows. Because of their long range, the interactions are weak, and we may try to apply the Landau kinetic equation. In its final form (6.34), as applied to a plasma, the interaction potential enters the collision term only through the constant $B^{\alpha\beta}$ defined in Eq. (6.30). The Fourier transform of the Coulomb potential (2.33): $V^{\alpha\beta}(r) = e_\alpha e_\beta / r$ is well-known:

$$\tilde{V}^{\alpha\beta}(k) = e_\alpha e_\beta \, \tilde{V}(k), \qquad \tilde{V}(k) = \frac{1}{2\pi^2 \, k^2}. \tag{8.1}$$

Inserting this form into (6.30) we obtain:

$$B^{\alpha\beta} \sim \int_0^\infty dk \, k^3 \left[\tilde{V}^{\alpha\beta}(k) \right]^2 \sim \int_0^\infty dk \, k^3 \, k^{-4} = \ln \infty - \ln 0 \,. \tag{8.2}$$

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We thus find a DIVERGENCE at both ends of the integration domain. Divergences often appear in theoretical physics, but never in the real world. The appearance of an infinity is always a signal of danger: some condition of validity is violated, and the problem must be reconsidered from the beginning in order to eliminate this unphysical feature.

As the wave vector k has the dimension of an inverse length, the divergence at large k corresponds to a divergence at short distances. This is no mystery. The pure Coulomb potential does not account for the complete interaction force of two charged particles: at very short distances a different, non-Coulombian repulsive interaction (of quantum mechanical origin) will dominate and produce the hard core existing for all types of atoms. If the hard core potential were properly taken into account, the problem could be treated in the Boltzmann manner (Chap. 7) and the divergence would no longer appear. It can even be shown that if the pure Coulomb problem is treated as a quantum mechanical weakly couples system there is no short range divergence: the quantum interference effects produce a natural cut-off. We therefore no longer discuss this aspect here.

The *long range divergence* is a much more serious problem. It is a characteristic feature of the Coulomb potential that appears not only in the classical Landau equation, but also in the quantum version as well as in the Boltzmann equation. In principle, it is due to the violation of Assumption C) requiring a finite range of the potential. Qualitatively speaking, if a given particle P feels the action of a partner Q located at a long distance, say r, it will also feel the action of many other particles located in a sphere of radius r around P. Such an effect is impossible if the dilute gas ordering (7.1) pertains: in order for particle P to feel the action of a partner, the latter must be at a maximum distance l_C . But this distance is much smaller than the average interparticle separation; there is no other particle within the range of action of P. The evolution is thus only due to binary collisions. In a plasma, the *collective effect* described above is unavoidable. Under these conditions, how can we still speak of localized collisions?

The hint towards the answer is provided by a kind of *self-healing effect* produced by the Coulomb interactions. This effect is known from equilibrium statistical physics, or even from macroscopic physics. An important point to be taken into account is the presence in a plasma of both positively and negatively charged particles in equal amounts, in order to ensure the *global electroneutrality*.[1] Consider again our central particle P, specified now as being a positive ion, and consider around it the sphere of radius r filled with electrons and ions. Although the plasma is supposed to be globally

---

[1] In recent, very elegant experiments, macroscopic samples of non-neutral plasmas are produced, confined and manipulated for long periods of time (hours). In spite of their great scientific interest, such situations are exceptional and exist only under very carefully controlled conditions. We shall not deal with such systems here.

homogeneous, the distribution of particles around a *fixed* ion is not homogeneous. Because of the electrostatic interactions, there is, on average, a greater chance of finding electrons than ions in the immediate neighbourhood of P. This effect is called the *polarization* of the medium by P; one also speaks of a *polarization cloud* formed around each particle. Thus, the particle Q (say, an ion) feels the repulsive action of the ion P, but also the action of the particles of its polarization cloud, which partially counteract the direct repulsion. As a result, the effective interaction between P and Q (in presence of the plasma) falls off much more rapidly than $1/r$: the interaction is *screened* by the particles of the medium.

This polarization effect was well known in equilibrium statistical mechanics of plasmas and electrolytes since the pioneering work of *Debye and Hückel* in 1923. Their approach was semi-phenomenological. They derived the electrostatic potential around particle P by writing a Poisson equation, combined with a self-consistent charge distribution given by Boltzmann's formula in terms of the potential itself. The idea is very similar to the one used later in non-equilibrium situations by Vlasov. An important step forward was done in 1950, when *J. Mayer* showed rigourously that the divergences appearing in the standard formulation of equilibrium statistical mechanics (in particular in the coefficients of the virial expansion that forms the basis of the non-ideal gas theory) could be suppressed by rearranging the virial series and performing a partial infinite summation of the most divergent terms. The rearranged series has finite coefficients and coincides, to leading order, with the Debye-Hückel theory. A similar equilibrium theory was developed for quantum plasmas by *Gell-Mann and Brueckner* and by *Sawada* in 1957. The first application of this type of reasoning to non-equilibrium plasmas was published independently by *R. Balescu* and by *A. Lenard* in 1961: their work will be reviewed here.[2]

In our preliminary discussion of Chap. 2, we recalled the main result of the Debye-Hückel equilibrium theory: the Coulomb potential is replaced by an effective interaction potential (2.36) behaving like

$$V^D(r) = e^2 \frac{\exp(-\kappa_D r)}{r} \,. \tag{8.3}$$

(In the forthcoming discussions of orders of magnitude, we suppress the species indices which do not play an essential role). The inverse Debye length $\kappa_D = r_D^{-1}$ is defined as:

$$\kappa_D = \left(\frac{4\pi e^2 n}{k_B T} \right)^{1/2} \,. \tag{8.4}$$

---

[2]The original papers treated the simpler model of a one-component plasma in presence of a neutralizing continuous background. We treat here the more realistic two-component electron-ion plasma model, using a simpler derivation than in the original papers.

Its Fourier transform is:

$$\tilde{V}^D(k) = \frac{e^2}{2\pi} \frac{1}{k^2 + \kappa_D^2}. \tag{8.5}$$

The Coulomb potential can be considered as a weak interaction; this means that e^2 is formally treated as a small parameter. More accurately, we define the dimensionless ratio of the interaction strength at the mean interparticle distance $n^{-1/3}$ to the thermal energy as the fundamental *plasma parameter* ρ. Its smallness characterizes the plasmas considered here (weakly coupled plasmas):

$$\rho \equiv \frac{e^2 n^{1/3}}{k_B T} \ll 1. \tag{8.6}$$

Comparing with (8.4) we see that this condition is equivalent (disregarding numerical factors of order one) to $\kappa_D^2 n^{-2/3} \ll 1$, or:

$$n r_D^3 \gg 1. \tag{8.7}$$

If r_D is interpreted as an effective interaction range, we could compare (8.7) to (7.1): the former seems to be the reverse of the latter, and could seem to be realized for high densities. This, however, is not the case, because r_D depends on the density. Clearly, the condition (8.6) is satisfied for low density and/or for high temperature. The plasmas used in thermonuclear fusion research and many astrophysical plasmas verify quite well the condition of small ρ. Actually, Eq. (8.7) says that the Debye length (i.e., the effective interaction range) should be much larger than the mean interparticle distance. This condition is necessary for the argument given above for the polarization to make sense: there must be many particles in the interaction sphere to provide a screening.

But the charge does not enter (8.3) only as the coupling strength e^2: it also enters the expression of κ_D. We note that this latter dependence of $V^D(r)$ on the charge appears through the combination $e^2 n$; this dependence is *non-analytic* [it involves $(e^2 n)^{1/2}$]. It follows that any perturbation theory involving a power series in e^2, truncated at a finite level, will miss the Debye screening effect. Our practical conclusion will thus be the following. In order to obtain a non-equilibrium theory consistent with the correct equilibrium plasma theory, we must formally *consider e^2 as a small parameter, but at the same time assume $(e^2 n)$ to be a finite quantity.* This practical rule is consistent with the basic condition (8.6) which implies:

$$\frac{e^6 n}{(k_B T)^3} \equiv (k_B T)^{-3} e^4 (e^2 n) \ll 1. \tag{8.8}$$

The smallness of this parameter is compatible with the smallness of e^2 and at the same time with the finiteness of $(e^2 n)$.

The interesting aspect of this practical criterion is that we have already seen in Sec. 7.1 that the two types of vertices appearing in the diagrams for the evolution of the correlation functions are well characterized from this point of view: the X-vertex are of order e^2 (i.e., λ), whereas the Y-vertex is of order $e^2 n$. We are thus able to select the appropriate diagrams on the basis of our new criterion.

8.2 The Integral Equation for the Correlation

We consider a fully ionized plasma, consisting of electrons and one species of singly charged ions, i.e., the same system that was treated in Secs. 5.3, 5.4. We use the same notations that were defined in Sec. 5.3, in particular, greek indices denote the species, e or i. The equation of evolution for the RDF is represented by the two diagrams of Fig. 4.4, which we reproduce here (Fig. 8.1).
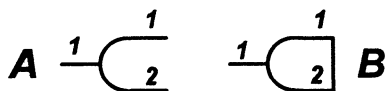
Figure 8.1. Diagrams for the evolution of the RDF for a plasma.

Both are Y-vertices, thus introducing the factor $(e^2 n)$ which is considered finite. If the RDF is taken of order zero, the dominant term will be the Vlasov term (A). The second term will be of order $(e^2 n)$ times the order of magnitude of the correlation function, which we now show to be of order $e^2 (e^2 n)^x$.

Among the diagrams of Fig. 4.5, the simplest is diagram A in Fig. 8.2: this represents an X-vertex acting on a product of RDF's: it is thus of order e^2, as stated above. Other diagrams of the same order are obtained by applying a Y-vertex $(e^2 n)$ to a product containing one correlation function (e^2). It is easily checked that the correlation functions of higher order are at most of order $e^4 (e^2 n)^x$.

Our selection criterion thus provided us once more with a closed set of equations for f and for g_2, which we write down explicitly [see Eqs. (4.41), (4.44)]:

$$(\partial_t - L_1^0) f^\alpha(x_1; t) = \sum_\beta \int dx_2 \left[L_{12}'^{\alpha\beta} f^\alpha(x_1; t) f^\beta(x_2; t) + L_{12}'^{\alpha\beta} g_2^{\alpha\beta}(x_1, x_2; t) \right] , \quad (8.9)$$

and:

$$(\partial_t - L_1^0 - L_2^0)\, g_2^{\alpha\beta}(x_1, x_2; t)$$
$$= L_{12}^{\prime\alpha\beta}\, f^\alpha(x_1; t) f^\beta(x_2; t)$$
$$+ \sum_\gamma \int dx_3 \left\{ L_{13}^{\prime\alpha\gamma} \left[f^\alpha(x_1; t) g_2^{\beta\gamma}(x_2, x_3; t) + f^\gamma(x_3; t) g_2^{\alpha\beta}(x_1, x_2; t) \right] \right.$$
$$\left. + L_{23}^{\prime\beta\gamma} \left[f^\beta(x_2; t) g_2^{\alpha\gamma}(x_1, x_3; t) + f^\gamma(x_3; t) g_2^{\alpha\beta}(x_1, x_2; t) \right] \right\} \qquad (8.10)$$
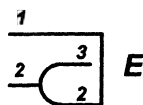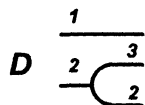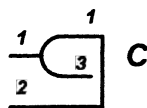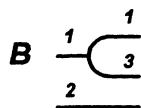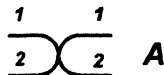
Figure 8.2. Diagrams for the evolution of the correlation function for a plasma.

The first steps of the solution are by now familiar. Eq. (8.10) is "solved" by convoluting the propagator $U_{12}^{0\alpha\beta}$ [Eqs. (5.13), (5.17)] with the right hand side: this operation actually transforms (8.10) into an integral equation, involving a time-integration from 0 to t. This expression is Markovianized by the same procedure as in Sec. 6.2 or 7.2: the delay in the source terms is neglected, and the integration domain is extended to infinity; moreover, the term involving the initial condition is neglected. This operation calls for a comment. The Markovianization in a weakly coupled system required the existence of a finite interaction range, l_C, hence of a finite duration of a collision, τ_C. In the present problem, the true Coulomb interaction has no finite range, but the *effective interaction* that will arise self-consistently from the theory does have such a finite range (in general). We thus *anticipate* the existence of an l_C, that must be verified *a posteriori*, and obtain asymptotically:

$$g_2^{\alpha\beta}(x_1, x_2; t) = \int_0^\infty d\tau\, U_{12}^{0\alpha\beta}(\tau) \left\{ L_{12}^{\prime\alpha\beta}\, f^\alpha(x_1; t) f^\beta(x_2; t) \right.$$
$$+ \sum_\gamma \int dx_3 \left(L_{13}^{\prime\alpha\gamma} \left[f^\alpha(x_1; t) g_2^{\beta\gamma}(x_2, x_3; t) + f^\gamma(x_3; t) g_2^{\alpha\beta}(x_1, x_2; t) \right] \right.$$
$$\left. \left. + L_{23}^{\prime\beta\gamma} \left[f^\beta(x_2; t) g_2^{\alpha\gamma}(x_1, x_3; t) + f^\gamma(x_3; t) g_2^{\alpha\beta}(x_1, x_2; t) \right] \right) \right\} \qquad (8.11)$$

From here on, we assume that the plasma is *spatially homogeneous*, hence:[3] $f^\alpha(x_1; t) = n\varphi^\alpha(\mathbf{v}_1; t) \equiv n\varphi^\alpha(1)$, and $g_2^{\alpha\beta}(x_1, x_2; t) = g_2^{\alpha\beta}(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; t)$. The treatment is made possible by using systematically a Fourier representation. We thus introduce the following abbreviated notation:

$$g_2^{\alpha\beta}(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; t) = \int d\mathbf{k} \, \exp\left[i\mathbf{k} \cdot (\mathbf{q}_1 - \mathbf{q}_2)\right] \widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2). \tag{8.12}$$

The reality of the correlation function implies:

$$\widetilde{g}^{\alpha\beta}(-\mathbf{k}; 1, 2) = \widetilde{g}^{*\,\alpha\beta}(\mathbf{k}; 1, 2) \tag{8.13}$$

(the star denotes complex conjugation). Next, we note that the interaction Liouvillian is expressed as follows [we note the special dependence of the interaction potential on the charges, Eq. (8.1)]:

$$\widetilde{L}_{12}^{\prime\alpha\beta} = e_\alpha e_\beta \int d\mathbf{k} \, \exp\left[i\mathbf{k} \cdot (\mathbf{q}_1 - \mathbf{q}_2)\right] \widetilde{V}(k) \, i\mathbf{k} \cdot \partial_{12}^{\alpha\beta}. \tag{8.14}$$

We use here the following symbol for the derivatives with respect to velocity, including the different masses of ions and electrons:

$$\partial_1^\alpha = \frac{1}{m_\alpha} \frac{\partial}{\partial \mathbf{v}_1}, \quad \partial_{12}^{\alpha\beta} = \frac{1}{m_\alpha} \frac{\partial}{\partial \mathbf{v}_1} - \frac{1}{m_\beta} \frac{\partial}{\partial \mathbf{v}_2}. \tag{8.15}$$

The Fourier transforms of the various terms in Eq. (8.11) are evaluated successively. The first term, corresponding to diagram A of Fig. 8.2 yields:

$$(A) = n^2 e_\alpha e_\beta \int_0^\infty d\tau \, \exp\left[-i\mathbf{k} \cdot (\mathbf{v}_1 - \mathbf{v}_2)\tau\right] \widetilde{V}(k) \, i\mathbf{k} \cdot \partial_{12}^{\alpha\beta} \, \varphi^\alpha(1)\varphi^\beta(2).$$

The second term, corresponding to diagram B in Fig. 8.2 yields:

$$(B) = 8\pi^3 n e_\alpha \sum_\gamma e_\gamma \int d\mathbf{v}_3 \int_0^\infty d\tau \, \exp\left[i\mathbf{k} \cdot (\mathbf{v}_1 - \mathbf{v}_2)\tau\right] \widetilde{V}(k) \, i\mathbf{k} \cdot \partial_1^\alpha \, \varphi^\alpha(1)\widetilde{g}^{\beta\gamma}(-\mathbf{k}; 2, 3).$$

The third term, corresponding to diagram C vanishes identically (for homogeneous systems):

$$(C) = 8\pi^3 n e_\alpha \sum_\gamma e_\gamma \int d\mathbf{v}_3 d\mathbf{l} \int_0^\infty d\tau \, \exp\left[i\mathbf{l} \cdot (\mathbf{v}_1 - \mathbf{v}_2)\tau\right] \delta(\mathbf{l}) \, \widetilde{V}(l) \, i\mathbf{l} \cdot \partial_1^\alpha \, \varphi^\gamma(3)\widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2$$

$$= 0$$

The diagram D is similar to B, and diagram E vanishes, like C. The τ−integrals are easily performed in terms of the $\delta_\pm$−distributions [Eq. (6.24) and (6.40)]. Collecting

---

[3]Note that, because of electroneutrality, the number densities of the electrons and of the ions are equal: $n_e = n_i = n$.

these partial results we obtain the asymptotic integral equation for the correlation (we introduce our usual notation for the relative velocity $\mathbf{g}_{12} = \mathbf{v}_1 - \mathbf{v}_2$):

$$
\begin{aligned}
\widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2) \;=\;& 8\pi^4 n e_\alpha \sum_\gamma e_\gamma \int d\mathbf{v}_3 \, \delta_-^*(\mathbf{k} \cdot \mathbf{g}_{12}) \, \widetilde{V}(k) \, i\mathbf{k} \cdot \partial_1^\alpha \, \varphi^\alpha(1) \widetilde{g}^{*\,\beta\gamma}(\mathbf{k}; 2, 3) \\
&+ 8\pi^4 n e_\beta \sum_\gamma e_\gamma \int d\mathbf{v}_3 \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \, \widetilde{V}(k) \left(-i\mathbf{k} \cdot \partial_2^\beta \right) \varphi^\beta(2) \widetilde{g}^{\alpha\gamma}(\mathbf{k}; 1, 3) \\
&+ \pi n^2 e_\alpha e_\beta \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \, \widetilde{V}(k) \, i\mathbf{k} \cdot \partial_{12}^{\alpha\beta} \, \varphi^\alpha(1) \varphi^\beta(2) \qquad (8.16)
\end{aligned}
$$

(the star denotes complex conjugation). The solution of this equation must be substituted into Eq. (8.9) in order to obtain the kinetic equation for homogeneous plasmas in the form:

$$
\begin{aligned}
\partial_t \varphi^\alpha(1) \;=\;& n^{-1} \sum_\beta \int d\mathbf{v}_2 \int d\mathbf{q}_2 \left[\nabla_1 V^{\alpha\beta}(\mathbf{q}_1 - \mathbf{q}_2) \right] \cdot \partial_1^\alpha \, g_2^{\alpha\beta}(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; t) \\
=\;& n^{-1} e_\alpha \sum_\beta e_\beta \int d\mathbf{v}_2 \, 8\pi^3 \int d\mathbf{k} \, \widetilde{V}(k) \left(-i\mathbf{k} \cdot \partial_1^\alpha \right) \widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2) \,. \qquad (8.17)
\end{aligned}
$$

We finally note that the RDF, and all factors in the first integral are real functions; in the second integral, $\widetilde{V}(k)$ is also real, but $\widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2)$ is a complex function, that can be represented as:

$$
\widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2) = \widetilde{g}_R^{\alpha\beta}(\mathbf{k}; 1, 2) + i \, \widetilde{g}_I^{\alpha\beta}(\mathbf{k}; 1, 2) \,. \qquad (8.18)
$$

It follows that only the imaginary part of the correlation contributes to (8.17):

$$
\partial_t \varphi^\alpha(1) = 8\pi^3 n^{-1} e_\alpha \sum_\beta e_\beta \int d\mathbf{v}_2 \int d\mathbf{k} \, \widetilde{V}(k) \, \mathbf{k} \cdot \partial_1^\alpha \, \widetilde{g}_I^{\alpha\beta}(\mathbf{k}; 1, 2) \,. \qquad (8.19)
$$

It is easily checked that if only the last term in Eq. (8.16) [i.e., diagram A in Fig. 8.2] is retained in the right hand side, the Landau kinetic equation (6.26) is recovered. In order to determine the collective effects in the collision term, we must solve the integral equation (8.16). In spite of its formidable aspect, it can be solved exactly, as will be shown in the next section.

8.3   The Plasma Kinetic Equation

The Fourier correlation function $\widetilde{g}^{\alpha\beta}(\mathbf{k}; 1, 2)$ is a function of three vector variables: $\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2$ and of the indices α, β. It should be realized, however, that we do not need all the information contained in this function. The kinetic equation (8.19) depends only on the simpler function:

$$\tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1) = \sum_\beta e_\beta \int d\mathbf{v}_2 \, \tilde{g}^{\alpha\beta}(\mathbf{k}; \mathbf{v}_1, \mathbf{v}_2) \,. \tag{8.20}$$

We note, moreover that the correlation function enters the right hand side of the integral equation (8.16) through the same combination. We therefore multiply both sides of that equation by e_β and integrate over $\mathbf{v}_2$, obtaining:

$$
\begin{aligned}
\tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1) &= 8\pi^4 n e_\alpha \sum_\beta e_\beta \int d\mathbf{v}_2 \, \delta_+(\mathbf{k} \cdot \mathbf{g}_{12}) \, \tilde{V}(k) \left[i\mathbf{k} \cdot \partial_1^\alpha \, \varphi^\alpha(1) \right] \tilde{G}^{*\beta}(\mathbf{k}; \mathbf{v}_2) \\
&\quad + 8\pi^4 n e_\alpha \sum_\beta e_\beta \int d\mathbf{v}_2 \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \, \tilde{V}(k) \left[-i\mathbf{k} \cdot \partial_2^\beta \, \varphi^\beta(2) \right] \tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1) \\
&\quad + \pi n^2 e_\alpha \sum_\beta e_\beta^2 \int d\mathbf{v}_2 \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \, \tilde{V}(k) \, i\mathbf{k} \cdot \partial_{12}^{\alpha\beta} \, \varphi^\alpha(1)\varphi^\beta(2) \tag{8.21}
\end{aligned}
$$

We introduce the following useful abbreviations:

$$d^\alpha(1) = 8\pi^3 n e_\alpha \, \tilde{V}(k) \left[\mathbf{k} \cdot \partial_1^\alpha \, \varphi^\alpha(1) \right] , \tag{8.22}$$

$$q^\alpha(1) = \pi n^2 e_\alpha \sum_\beta e_\beta^2 \int d\mathbf{v}_2 \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \, \tilde{V}(k) \, i\mathbf{k} \cdot \partial_{12}^{\alpha\beta} \, \varphi^\alpha(1)\varphi^\beta(2) , \tag{8.23}$$

$$\varepsilon(1) = 1 + 8\pi^4 n \tilde{V}(k) \sum_\beta e_\beta^2 \int d\mathbf{v}_2 \, \delta_-(\mathbf{k} \cdot \mathbf{g}_{12}) \left[i\mathbf{k} \cdot \partial_2^\beta \, \varphi^\beta(2) \right] \tag{8.24}$$

It is easily checked that the function $\varepsilon(1)$ is precisely the dielectric function $\varepsilon(\mathbf{k}, z)$, (5.49) that appeared in the theory of the Vlasov equation, evaluated for $z = \mathbf{k} \cdot \mathbf{v}_1 + i\epsilon$ [where ϵ is an infinitesimal positive number, see Eq. (6.43)]. It should be stressed, however, that this quantity is evaluated with an arbitrary velocity distribution $\varphi^\beta(2)$, instead of the equilibrium distribution $\varphi_0^\beta(2)$ as in (5.49).

Eq. (8.21) is now rewritten as:

$$\varepsilon(1)\tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1) = i\pi \, d^\alpha(1) \sum_\beta e_\beta \int d\mathbf{v}_2 \, \delta_+(\mathbf{k} \cdot \mathbf{g}_{12}) \, \tilde{G}^{*\beta}(\mathbf{k}; \mathbf{v}_2) + q^\alpha(\mathbf{k}; \mathbf{v}_1) \,. \tag{8.25}$$

We reduced our problem to an integral equation for a complex function of a single vector variable $\mathbf{v}_1$ and an index α ($\mathbf{k}$ is merely a parameter). The similarity of this equation with the solution (5.51) of the linearized Vlasov equation is remarkable. The kinetic equation involves the imaginary part of $\tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1)$ as follows:

$$\partial_t \varphi^\alpha(1) = 8\pi^3 n^{-1} e_\alpha \int d\mathbf{k} \, \tilde{V}(k) \, \mathbf{k} \cdot \partial_1^\alpha \, \tilde{G}_I^\alpha(\mathbf{k}; \mathbf{v}_1) \,. \tag{8.26}$$

Next, we note that $\tilde{G}^\alpha(\mathbf{k}; \mathbf{v}_1) \equiv G^\alpha(1)$, as well as $q^\alpha(1)$ and $d^\alpha(1)$ depend on the vector variable $\mathbf{v}_1$, that is, on three scalar variables. But the kernel of the integral equation (8.25), $\delta_+(\mathbf{k} \cdot \mathbf{v}_1 - \mathbf{k} \cdot \mathbf{v}_2)$ depends on $\mathbf{v}_1$ and $\mathbf{v}_2$ only through their projection on $\mathbf{k}$; the perpendicular components of $\mathbf{v}_2$ are simply integrated out. Similarly, the dielectric function $\varepsilon(1)$ only depends on $\mathbf{k} \cdot \mathbf{v}_1$. We denote the parallel component of the velocity by ν:

$$\nu = \frac{\mathbf{k} \cdot \mathbf{v}}{k} . \tag{8.27}$$

Moreover, with every function $f^\alpha(\mathbf{v})$ of $\mathbf{v}$ and α we associate a function $\overline{f}(\nu)$ of the single variable ν:

$$\overline{f}(\nu) = \sum_\alpha e_\alpha \int d\mathbf{v}\, \delta \left(\nu - \frac{\mathbf{k} \cdot \mathbf{v}}{k} \right) f^\alpha(\mathbf{v}) . \tag{8.28}$$

We define in this way the functions $\overline{G}(\nu)$, $\overline{q}(\nu)$ and $\overline{d}(\nu)$ and note the important relation:

$$\frac{\pi}{k} \overline{d}(\nu) = \varepsilon_I(\nu) . \tag{8.29}$$

We also note that the function $\overline{q}(\nu)$ is real, i.e.:

$$\overline{q}_I(\nu) = 0 . \tag{8.30}$$

Multiplying both sides of Eq. (8.25) by $e_\alpha \delta\left(\nu_1 - \mathbf{k} \cdot \mathbf{v}_1/k\right)$ and integrating over $\mathbf{v}_1$ we obtain:

$$\varepsilon(\nu_1)\, \overline{G}(\nu_1) = i\varepsilon_I(\nu_1) \int d\nu_1\, \delta_+(\nu_1 - \nu_2)\, \overline{G}^*(\nu_2) + \overline{q}(\nu_1) . \tag{8.31}$$

This one-dimensional integral equation is much simpler than (8.25). It is important to note that if (8.31) is solved, we automatically obtain the solution of (8.25) as well. Indeed, using the obvious relation:

$$\sum_\beta e_\beta \int d\mathbf{v}_2\, \delta_+(\mathbf{k} \cdot \mathbf{g}_{12})\, G^{*\beta}(\mathbf{k}; \mathbf{v}_2) = k^{-1} \int d\nu_1\, \delta_+(\nu_1 - \nu_2)\, \overline{G}^*(\nu_2) ,$$

we can eliminate the integral between Eqs. (8.25) and (8.31) and obtain the following simple algebraic relation between G^α and $\overline{G}$:

$$G^\alpha(1) = \frac{\pi\, d^\alpha(1)}{k\, \varepsilon_I(\nu_1)}\, \overline{G}(\nu_1) + \frac{1}{\varepsilon(\nu_1)} \left[q^\alpha(1) - \frac{\pi\, d^\alpha(1)}{k\, \varepsilon_I(\nu_1)}\, \overline{q}(\nu_1) \right] \tag{8.32}$$

In particular, the imaginary part needed for the kinetic equation is:

$$G_I^\alpha(1) = \frac{\pi\, d^\alpha(1)}{k\, \varepsilon_I(\nu_1)}\, \overline{G}_I(\nu_1)$$
$$+ \frac{1}{|\varepsilon(\nu_1)|^2}\left[\varepsilon_R(\nu_1)q_I^\alpha(1) - \varepsilon_I(\nu_1)q_R^\alpha(1) + \frac{\pi\, d^\alpha(1)}{k}\, \overline{q}_R(\nu_1)\right]$$

The expression in square brackets is worked out by using the explicit expressions (8.22) - (8.24): many cancellations occur and we are left with:

$$G_I^\alpha(1) = \frac{\pi\, d^\alpha(1)}{k\, \varepsilon_I(\nu_1)}\, \overline{G}_I(\nu_1) + \frac{q_I^\alpha(1)}{|\varepsilon(\nu_1)|^2}\,. \tag{8.33}$$

We now split split Eq. (8.31) into real and imaginary components, using all the previous results:

$$\varepsilon_R \overline{G}_I - \varepsilon_I \mathcal{P}\overline{G}_I = 0\,, \tag{8.34}$$

$$\varepsilon_R \overline{G}_R + \varepsilon_I \mathcal{P}\overline{G}_R = \overline{q}_R + 2\varepsilon_I \overline{G}_I\,. \tag{8.35}$$

We introduced here the following notation for the principal part:

$$\mathcal{P}f = \frac{1}{\pi}\mathcal{P}\int d\nu'\, \frac{f(\nu')}{\nu - \nu'}\,.$$

Eq. (8.34) for the imaginary part of $\overline{G}$ is decoupled from the equation for the real part [because of (8.29)]. This is very helpful: for the derivation of the kinetic equation we only require $\overline{G}_I$, hence we need not consider at all Eq. (8.35). Eq. (8.34) is called a *singular integral equation of Hilbert type*: a well studied class of equations. The important point for us is that it is a homogeneous equation [because of (8.30)]. It thus possesses the trivial solution. It can be shown, moreover, that under a certain condition on the RDF, this is the only solution. We do not give here the proof of this property, which requires a deeper analysis of the singular integral equation (see **BN8**). In conclusion, the solution of (8.34) is simply:

$$\overline{G}_I(\nu) = 0\,. \tag{8.36}$$

This result is substituted into Eq. (8.33), thus obtaining:

$$\tilde{G}_I^\alpha(\mathbf{k}; \mathbf{v}_1) = \frac{\tilde{q}_I^\alpha(\mathbf{k}; \mathbf{v}_1)}{|\varepsilon(\nu_1)|^2}\,. \tag{8.37}$$

Finally, substitution of this result in (8.26) and use of (8.23) yields:

$$\partial_t \varphi^\alpha(\mathbf{v}_1; t) = 8\pi^4 n e_\alpha^2 \sum_\beta e_\beta^2 \int d\mathbf{v}_2 \int d\mathbf{k} \ \mathbf{k} \cdot \partial_1^\alpha$$

$$\times \frac{\tilde{V}^2(k)}{|\varepsilon(\nu_1)|^2} \ \delta(\mathbf{k} \cdot \mathbf{g}_{12}) \ \mathbf{k} \cdot \partial_{12}^{\alpha\beta} \ \varphi^\alpha(\mathbf{v}_1; t)\varphi^\beta(\mathbf{v}_2; t) \ . \tag{8.38}$$

This is the final form of the *kinetic equation for plasmas*, usually called in the literature the BALESCU-LENARD *kinetic equation.*

8.4   Properties of the Balescu-Lenard Equation

Given the complicated form of the starting equations, the final form of the kinetic equation is surprisingly simple! Its form is, superficially, identical with the Landau equation (6.26), in which the Coulomb potential is replaced by an effective potential:

$$\tilde{V}_{eff}^{\alpha\beta}(k; \mathbf{k} \cdot \mathbf{v}) = e_\alpha e_\beta \frac{\tilde{V}(k)}{\varepsilon(k; \mathbf{k} \cdot \mathbf{v})} . \tag{8.39}$$

The physical interpretation is thus very simple and satisfactory. The plasma appears as a weakly coupled system, in which the collisions are due to the interactions via an effective, screened potential. This allows us to understand *a posteriori the possibility of speaking of localized collisions* and of a finite effective range of the interactions. It must be stressed that the effective potential is not an *ad hoc* construct: the screening has been *derived* exactly from the dynamical laws, including the collective effects.

As a result of this formal similarity, the Balescu-Lenard equation shares with the Landau equation all the properties of a true kinetic equation. The proof of these general properties is the same as for the Landau equation, and will be discussed in Chap. 9.

In spite of this formal similarity, there is a very essential difference between the Balescu-Lenard equation and the Landau equation: the former is *much more strongly nonlinear*. Indeed, as explained after Eq. (8.24), the dielectric constant appearing in (8.39) is evaluated with the *unknown distribution function* $\varphi(\mathbf{v}, t)$. Thus, the polarization cloud producing the screening is not considered as given and static, as in the linearized Vlasov equation studied in Sec. 5.4, but appears as a functional of the instantaneous state of the plasma, evolving in time. It can be said that the kinetic equation is "infinitely nonlinear", as compared with the quadratic nonlinearity of the Landau equation. This feature expresses the fact that the long-range Coulomb potential produces truly collective collisions, involving (in principle) all the particles of the medium. This introduces, of course, an enormous mathematical complication. The full nonlinear study of the Balescu-Lenard equation has not yet been tackled.

Whereas this equation yields a very clear and simple physical picture, it can only be taken as a starting point for further approximations when it is used for explicit calculations. We now show, in particular, in what sense the Landau equation can be considered as an approximation to the Balescu-Lenard equation.

Consider, as an example, the distribution function (5.58) which is, in its bulk, i.e. for small velocities, an approximation to a Maxwellian. The parameter u_0 can thus be interpreted as the thermal velocity, $u_0 \approx (k_B T/m)^{1/2}$. The corresponding dielectric function (for singly charged ions) was calculated in (5.60):

$$\varepsilon(k; z) = 1 - \frac{4\pi e^2 n}{m\,k^2} \frac{1}{\left(i\sqrt{\dfrac{k_B T}{m}} + \dfrac{z}{k}\right)^2}. \tag{8.40}$$

The limit of this expression for $z \to 0$ is:

$$\varepsilon_D(k) = 1 + \frac{4\pi e^2 n}{k_B T\,k^2} = 1 + \frac{\kappa_D^2}{k^2}. \tag{8.41}$$

If this equation is substituted into (8.39), the effective interaction potential reduces to the Debye potential (8.5). The limit $z \to 0$ corresponds to the limit $t \to \infty$ for the inverse Laplace transform of the effective potential. The latter is, in general a time-dependent function (see Sec. 5.4); the limiting static expression is reached when all the transient oscillations have been damped.

In connection with the kinetic equation, the static limit can also be interpreted in an alternative way. The dielectric function entering (8.39) is evaluated at $z = \mathbf{k} \cdot \mathbf{v}$; hence the limit $z \to 0$ is also a limit $v \to 0$. Thus, the static limit expresses the contribution to the effective potential of the low-velocity particles in the bulk of the distribution function. Clearly, this limiting potential no longer depends on the unknown distribution function. The infinitely nonlinear Balescu-Lenard equation is reduced to the quadratically nonlinear Landau equation. The conclusion is that *whenever the large-velocity population is (e.g.) exponentially small compared to the bulk, the Landau equation evaluated with a Debye potential is an acceptable approximation of the plasma kinetic equation.* On the contrary, whenever there is a long tail, or a bump in the tail of the velocity distribution, one may expect non-negligible differences with respect to the Landau equation. It is known, for instance, that under certain conditions, a "bump-in-tail" distribution may lead to a microscopic instability of the plasma: in that case the derivation of the kinetic equation must be modified and the equation itself takes a different form. This is just one example of a host of nonlinear effects that can be expected, but which are still open for investigation.

In practice, the static approximation of the plasma kinetic equation amounts to using the Landau equation with a Debye potential (8.5). This is not sufficient, however, for obtaining a finite coefficient B in Eq. (6.30): there remains a divergence for large

k (i.e., small distance). This is due to the absence of a hard core in this potential. A general kinetic equation combining the Boltzmann and the Balescu-Lenard equation can be derived. We do not discuss this rather complicated result here, but rather give a phenomenological solution. The integral $B^{\alpha\beta}$ in Eq. (6.34) is evaluated for a Debye potential, with a cut-off at $k = k_M$:

$$B^{\alpha\beta} = 8\pi^5 e_\alpha e_\beta \int_0^{k_M} dk \left[\widetilde{V}^D(k)\right]^2 k^3. \tag{8.42}$$

On a physical basis, the cut-off k_M is chosen as the inverse distence of closest approach at which a collision produces a deflection of 90°: this turns out to be:

$$k_M = \frac{3T}{e^2}. \tag{8.43}$$

Although this choice may seem somewhat arbitrary, it should be noted that the result for B is not very sensitive to the exact value, because the divergence is only logarithmic. Using this result, we find:

$$B^{\alpha\beta} = 2\pi e_\alpha^2 e_\beta^2 \ln\Lambda, \tag{8.44}$$

where the *Coulomb logarithm* is defined (for singly charged ions) as:

$$\ln\Lambda = \ln\frac{3T}{e^2 \kappa_D}. \tag{8.45}$$

Note that this quantity is weakly (logarithmically) dependent on the temperature and on the density. The approximation scheme described here is widely used in plasma kinetic theory.

8.5   Bibliographical Notes BN8

The first, semi-phenomenological treatment of collective effects for charged particles was the classical *theory of electrolyte solutions:*

Debye, P. and Hückel, E., 1923, Physik. Z., **24**, 185;

This work was followed by an enormous literature in physical chemistry.

The first *equilibrium theory* of systems of charged particles, based on rigourous equilibrium classical statistical mechanics was:

Mayer, J., 1950, J. Chem. Phys., **18**, 1426.

The *equilibrium theory of quantum plasmas* was first obtained in the following works:

Gell-Mann, M. and Brueckner, K.A., 1957, Phys. Rev., **106**, 364,

Sawada, K., 1957, Phys. Rev., **106**, 372.

The *plasma kinetic equation* was obtained independently in 1960 by:

Balescu, R., 1960, Phys. Fluids, **3**, 52,

Lenard, A., 1960, Ann. Phys. (N.Y.), **3**, 390.

It was also obtained independently by R.L. Guernsey, who unfortunately never published the result formally:

Guernsey, R.L., 1960, *The kinetic theory of fully ionized gases*, Off. Naval Res., Contract No. Nonr. 1224 (15).

The integral equation (8.25) was obtained in 1946 by N.N. Bogolioubov **(BN5)**: he did not, however, solve this equation and did not obtain an explicit kinetic equation.

Among the textbooks and monographs discussing this equation, we mention the following ones:

Balescu, R., 1963, **RB-1, (BN1)**

Montgomery, D.C. and Tidman, D., 1964, *Plasma Kinetic Theory*, McGraw Hill, New York,

Klimontovich, Yu.L., 1964, **(BN6)**,

Klimontovich, Yu.L., 1982, *Kinetic Theory of Nonideal Gases and Nonideal Plasmas*, Pergamon, Oxford,

Nicholson, D., 1983, **(BN5)**.

The extension of the kinetic equation to the case of an *unstable plasma* was done in:

Balescu, R., 1963, J. Math. Phys., 4, 1009,

Frieman, E.A. and Rutherford, P., 1963, Phys. Fluids, **6**, 67; 1964, Ann. Phys. (N.Y.), **28**, 134.

The best book on the mathematical theory of the singular integral equations is:

Muskhelishvili, N.I., 1953, **(BN6)**;   see also:

Mikhlin, S.G., 1950, *Singular Integral Equations*, Amer. Math. Soc. Translations, no. 24,

Gakhov, F.D., 1958, *Kraevye Zadachi* (Boundary Problems, in russian), Fizmatgiz, Moscow

Chapter 9

Properties of Kinetic Equations

9.1   The Concept of a Kinetic Equation

The equations of evolution for the reduced one-particle distribution function (RDF) presented in Chaps. 6-8 were derived from the exact dynamical Liouville equation, via the BBGKY hierarchy and the correlation dynamics, by specifying as precisely as possible a set of well-defined approximations, which were summarized in Sec. 6.4. for the case of a weakly coupled gas. The second of these assumptions can be modified in order to lead to other equations. We thus summarize these conditions in a slightly more general form:

- A) *The thermodynamic limit:* $N \to \infty$, $V \to \infty$, $N/V = n = const.$;

- B) *Existence of a small parameter characteristic of the system;*

- C) *Finite range of the interactions and of the correlations;*

- D) *Specific ordering of the length- and time-scales:* $l_C \ll l_{mfp} \ll l_H$, $\tau_C \ll \tau_R \ll \tau_H$;

- E) *Asymptotic treatment of the equations of evolution:* $t \gg \tau_C$.

The result of the implementation of assumptions A) - E) is the appearance of a COLLISION TERM in the *closed* equation of evolution of the RDF $f(\mathbf{q}, \mathbf{v}; t)$. Such an equation of evolution, including the collision term, is called a KINETIC EQUATION.

The Landau equation derived in Chap. 6 is the simplest representative of this class, and will be considered as a paradigmatic kinetic equation.The kinetic equation for a weakly coupled system is, however, not the only one of its kind. By choosing different parameters in assumption B), a whole *class of kinetic equations* can be

derived, describing many different physical systems. Two of them were considered in Chaps. 7 and 8. The common properties of all the kinetic equations are consequences of the assumptions A), C) - E): they are discussed below.

A first striking feature is the following: the kinetic equations are CLOSED *equations of evolution for the RDF* $f(\mathbf{q}, \mathbf{v}; t)$. This feature contrasts with the BBGKY equations (4.28) - (4.30) or the correlation equations (4.41), (4.44): these have a hierarchical structure, hence forming an infinite set of equations in the thermodynamic limit. The hierarchy has been truncated at the level of the two-particle correlation as a result of assumption B). In the remaining *finite* set of equations, the correlations are eliminated by solving for g_2 in terms of f. The type of closure depends, of course, on ~~the choice of the smallness~~ parameter. Attempts at a general formulation of kinetic theory independent of closure assumptions ~~will be briefly discussed in Chap. 16~~; in spite of their theoretical interest, such treatments are essentially formal constructions. It remains true that an *explicit* kinetic equation can only be derived whenever some form of closure is possible.

The next conspicuous property of the kinetic equations is their NONLINEAR *character*. This reflects the necessary role of the *interactions* in the evolution process. In a theory involving only one-particle RDF's, an s–particle interaction process is represented by a functional of a *product* of s RDF's. This again contrasts with the BBGKY formulation which is a linear set of equations, involving many (in principle, infinitely many) different distribution functions; hence an s-particle process involves a *single* function f_s. The presence of interactions is, however, not a sufficient condition for an equation of evolution to qualify as a kinetic equation describing a collision process.

A third common property is the MARKOVIAN *character* of the evolution process described by these equations: This is in contrast to the exact master equations (6.4) or (7.7). The "Markovianization" (see Sec. 6.2) is a result of the existence of widely separated length- and time-scales and of the asymptotic treatment, hence of Assumptions A), C) - E). Thus, the rate of change of the RDF at time t only depends on the value of $f(\mathbf{q}, \mathbf{v}; t)$, and not on the previous history.

The result of the consistent implementation of the assumptions A) - E) is therefore the appearance of a new type of equation of evolution. As will be shown below, the type of evolution described by the asymptotic kinetic equations has many features in common with a probabilistic process, in contrast to a purely dynamical law. *A crucial point in statistical dynamics has been reached here. From the* REVERSIBLE, DETERMINISTIC *dynamics, an* IRREVERSIBLE, STOCHASTIC *evolution law has emerged.* We do not claim to have obtained here the final solution of the paradox of irreversibility. But, for all systems to which assumptions A) - E) are applicable, we do have a solution to this problem. Before continuing our analysis of the kinetic equations, it is appropriate to briefly review some aspects of the theory of stochastic processes.

Additional aspects of this theory will be studied in forthcoming chapters.

9.2   Stochastic Equations of Evolution

Let y denote a variable in which we are interested: it could be, for instance, the position or the velocity of a particle. If y were a deterministic quantity obeying a dynamical law, we could construct a function of time $y(t)$, which determines a well-defined value of y at every time t, given appropriate initial data $y(0) = y_0$: this function is called a *trajectory*, or an *orbit*. But if y is a *random variable*, such a function does not exist. At every given time, the variable y can take *any value whatsoever* within its range of variation. Another way of looking at this situation is as follows. In a first experiment, the system starting at $y = y_0$ follows a well defined orbit, or *sample path*: $y_1(t)$, as described above. But, if the experiment is repeated, starting from the same initial condition, the sample path of a random variable (in contrast to a deterministic one) will be different in each *realization*. However, at every time t, there is a certain probability (in the range $[0, 1]$) attached to every possible value of y. (Alternatively, a probability is ascribed to each sample path). If we assume that y is a continuous variable, we should rather speak about probability densities. To be precise, we define the *probability density* $p(y; t)$ of the random variable y at time t by stating that the probability of finding the value of the variable in the infinitesimal interval $(y, y + dy)$ is $p(y; t)\, dy$. Note that the concept of a random variable includes the deterministic variable as a special case. If, indeed, a trajectory $y(t)$ exists, the corresponding probability density is: $p_D(y; t) = \delta[y - y(t)]$. This singular limit expresses the fact that the whole probability is concentrated along the deterministic orbit.

The knowledge of the function $p(y; t)$ is not sufficient, in general, for the complete characterization of the evolution process. Consider an ordered sequence of times: $t_n \geq t_{n-1} \geq ... \geq t_1$ and let $p_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1)$ be the *joint probability density*, i.e., the probability density of jointly finding the value y_n at time t_n, the value y_{n-1} at time t_{n-1}, etc. Clearly, this joint probability cannot be inferred from the mere knowledge of $p(y; t)$ because there is a *correlation* between what happens at time t_1 and at time t_2, etc. The function $p_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1)$ may, however, in certain cases, be expressed in terms of lower order joint probabilities.

The simplest case is the so-called *purely random process*, in which the knowledge of $p_1(y; t) \equiv p(y; t)$ is, indeed, sufficient for the determination of the process. This fact is expressed by the following factorization property, which tells us that whatever happens at time t is independent of what happened at any earlier time:

$$p_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1) = p(y_n; t_n)\, p_{n-1}(y_{n-1}; t_{n-1} | ... | y_1; t_1), \quad \forall n,$$

which, in turn, implies:

$$p_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1) = \prod_{k=1}^{n} p(y_k; t_k). \tag{9.1}$$

This would, however, be a very unrealistic assumption in a continuous physical process: for short enough time intervals there must be a causal relationship between successive events.

The next simplest case is the only one which will be considered here, because of its fundamental importance for statistical dynamics: it is called the **MARKOV PROCESS**. The whole information is now contained in the first two functions $p_1 \equiv p$, p_2. We introduce the concept of a *transition probability* $w_2(y_2; t_2 | y_1; t_1)$ defined by the following relation:

$$p_2(y_2; t_2 | y_1; t_1) = w_2(y_2; t_2 | y_1; t_1) \, p(y_1; t_1). \tag{9.2}$$

Thus, the joint probability density of finding y_1 at t_1 and y_2 at t_2 equals the probability density of finding y_1 at t_1 times the probability of a transition from y_1 at t_1 to y_2 at t_2 [remember: $t_2 \geq t_1$]. The transition probability has the following properties:

$$w_2(y_2; t_2 | y_1; t_1) \geq 0, \tag{9.3}$$

$$\int dy_2 \, w_2(y_2; t_2 | y_1; t_1) = 1, \tag{9.4}$$

$$\int dy_1 \, w_2(y_2; t_2 | y_1; t_1) \, p(y_1; t_1) = p(y_2; t_2). \tag{9.5}$$

We also consider the *n-th order transition probability* $w_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1)$, defined as the *conditional* probability density of finding the value y_n at time t_n, given that y had the values $y_{n-1}, y_{n-2}, ..., y_1$ at the respective earlier times $t_{n-1}, t_{n-2}, ..., t_1$. A *Markov process* is defined by the condition:

$$w_n(y_n; t_n | y_{n-1}; t_{n-1} | ... | y_1; t_1) = w_2(y_n; t_n | y_{n-1}; t_{n-1}), \quad n \geq 2. \tag{9.6}$$

This equation says that, for a Markov process, the probability of a transition at time t_{n-1} from a value y_{n-1} to a value y_n at time t_n depends (besides on y_n, t_n) only on the value of y at the time t_{n-1} of the transition, and *not at all on the previous history of the system*.

It is easily shown (and intuitively clear) that the transition probability for a Markov system obeys the following equation:

$$w_2(y_3; t_3 | y_1; t_1) = \int dy_2 \, w_2(y_3; t_3 | y_2; t_2) \, w_2(y_2; t_2 | y_1; t_1). \tag{9.7}$$

This fundamental integral equation, called the CHAPMAN-KOLMOGOROV EQUATION, can be taken as an alternative definition of a Markov process. It says that the probability of a transition from y_1 at t_1 to y_3 at t_3 can be obtained by taking the product of the transition probability to some value y_2 at some intermediate time t_2 and the transition probability from that value to the final one at t_3, and summing over all possible intermediate values of y.

We consider two important consequences of the Chapman-Kolmogorov equation, combined with some additional assumptions. We first note that the natural "initial condition" for w_2 is:

$$w_2(y_2; t_1|y_1; t_1) = \delta(y_2 - y_1). \tag{9.8}$$

We assume now that the transition probability from a state y_1 to a *different* state y_2 in a sufficiently short time interval $t_2 - t_1 = \Delta t$ is proportional to Δt; thus:

$$w_2(y_2; t_1 + \Delta t |y_1; t_1) = A\,\delta(y_2 - y_1) + \Delta t\,W_{t_1}(y_2|y_1). \tag{9.9}$$

$W_t(y_2|y_1)$ is naturally called the *transition probability per unit time*. The first term in the right hand side represents the probability that the random variable remains in y_1 during the interval Δt; the factor A is determined by the normalization condition (9.4):

$$A = 1 - \Delta t \int dy_2\, W_{t_1}(y_2|y_1). \tag{9.10}$$

We now write the Chapman-Kolmogorov equation (9.7), setting $y_3 = y$, $t_3 = t + \Delta t$, $y_2 = y'$, $t_2 = t$; we then expand the left hand side to first order in Δt around $t_3 = t$, use Eqs. (9.9) and (9.10) and take the limit $\Delta t \to 0$, obtaining:

$$
\begin{aligned}
\partial_t w_2(y; t\,|\,y_1; t_1) &= -w_2(y; t\,|\,y_1; t_1) \int dy'\, W_t(y'\,|\,y) \\
&\quad + \int dy'\, W_t(y\,|\,y')\, w_2(y'; t\,|\,y_1; t_1)
\end{aligned}
\tag{9.11}
$$

This equation is transformed into an equation for the probability density $p(y; t)$ by multiplying both sides by $p(y_1; t_1)$ and using Eq. (9.5):

$$\partial_t p(y; t) = \int dy'\,\left[-W_t(y'|y)\,p(y; t) + W_t(y|y')\,p(y'; t)\right]. \tag{9.12}$$

This is the first type of stochastic equation of great importance in statistical dynamics. It is called a GAIN-LOSS EQUATION or, in the literature on stochastic processes, the MASTER EQUATION.[1] It says that the probability of being in state y changes in time for two reasons:

---

[1] We shall not use this name, in order to avoid confusion with the non-markovian master equations (6.4) or (7.7) introduced in previous chapters.

a) The system being in state y leaves it and goes to a different state y' with a probability $W_t(y'|y)$ per unit time; this represents a *loss* for state y.

b) The system being in any other state y' makes a transition towards y with a probability $W_t(y|y')$ per unit time; this represents a *gain* for state y.

We now perform a different transformation of the Chapman-Kolmogorov equation, by using an alternative set of hypotheses. We first assume that the transition probability $w_2(y_2; t + \Delta t | y_1; t)$ does not depend on the time t at which the transition occurs, but only on the time interval Δt; we thus write:

$$w_2(y_2; t + \Delta t \mid y_1; t) = w(y_2 \mid y_1; \Delta t) \qquad (9.13)$$

Under this condition the stochastic process is called *stationary*. An equation of evolution for w can be obtained under certain conditions; for mathematical "safety", the derivation will be done in a "weak sense", i.e. in the sense of distributions. Let $R(y)$ be an arbitrary, regular function of y, and consider the following expression:

$$\int dy\, R(y)\, \frac{\partial w(y|x; \tau)}{\partial \tau}$$
$$= \lim_{\Delta\tau \to 0} (\Delta\tau)^{-1} \int dy\, R(y)\, [w(y|x; \tau + \Delta\tau) - w(y|x; \tau)]$$
$$= \lim_{\Delta\tau \to 0} (\Delta\tau)^{-1} \int dy\, R(y)\, \left[\int dz\, w(y|z; \Delta\tau)\, w(z|x; \tau) - w(y|x; \tau)\right], \quad .$$

where the Chapman-Kolmogorov equation (9.7) was used in the last step. In the first term we interchange the order of integrations and expand $R(y)$ in a Taylor series around $y = z$; the zeroth order term is cancelled by the last term of the integrand, and we are left with:

$$\int dy\, R(y)\, \frac{\partial w(y|x; \tau)}{\partial \tau}$$
$$= \lim_{\Delta\tau \to 0} (\Delta\tau)^{-1} \left\{ \int dz\, \frac{\partial R(z)}{\partial z}\, w(z|x; \tau) \int dy\, (y - z)\, w(y|z; \Delta\tau) \right.$$
$$\left. + \tfrac{1}{2} \int dz\, \frac{\partial^2 R(z)}{\partial z^2}\, w(z|x; \tau) \int dy\, (y - z)^2\, w(y|z; \Delta\tau) + ... \right\}. \qquad (9.14)$$

We now make the following basic assumptions:

$$\int dy\, (y - z)\, w(y|z; \Delta\tau) \;\equiv\; \langle \Delta z \rangle = A(z)\, \Delta\tau + O\left[(\Delta\tau)^2\right],$$
$$\int dy\, (y - z)^2\, w(y|z; \Delta\tau) \;\equiv\; \left\langle (\Delta z)^2 \right\rangle = B(z)\, \Delta\tau + O\left[(\Delta\tau)^2\right],$$
$$\int dy\, (y - z)^n\, w(y|z; \Delta\tau) \;=\; O\left[(\Delta\tau)^2\right], \quad n \geq 3. \qquad (9.15)$$

These averages are called *transition moments*. The orders of magnitude postulated here are obtained in many important physical examples (they may be generalized, with a more complicated final result). The limits in Eq. (9.14) can now be calculated explicitly:

$$\int dy\, R(y)\, \frac{\partial w(y|x;\tau)}{\partial \tau}$$
$$= \int dz\, w(z|x;\tau) \left\{ \frac{\partial R(z)}{\partial z}\, A(z) + \frac{1}{2}\, \frac{\partial^2 R(z)}{\partial^2 z}\, B(z) \right\}$$

This result is integrated by parts, and all terms are grouped as follows:

$$\int dy\, R(y) \left\{ \frac{\partial w(y|x;\tau)}{\partial \tau} + \frac{\partial}{\partial y}\, [A(y)\, w(y|x;\tau)] - \frac{1}{2}\, \frac{\partial^2}{\partial y^2}\, [B(y)\, w(y|x;\tau)] \right\} = 0\,.$$

As this expression must be zero, whatever the function $R(y)$, we conclude that the bracketted expression must vanish. This yields an equation of evolution for $w(y|x;\tau)$, which can be transformed into an equation for the probability density by the same procedure as in the passage from (9.11) to (9.12):

$$\frac{\partial p(y;t)}{\partial t} = -\frac{\partial}{\partial y}\, [A(y)\, p(y;t)] + \frac{1}{2}\, \frac{\partial^2}{\partial y^2}\, [B(y)\, p(y;t)]\,. \tag{9.16}$$

This is the celebrated FOKKER-PLANCK EQUATION, that plays a major role in statistical dynamics. It is often written in a slightly different form, by introducing the quantities:

$$D(y) = \frac{1}{2}\, \frac{\left\langle (\Delta y)^2 \right\rangle}{\Delta \tau}\,, \tag{9.17}$$

$$F(y) = -\frac{\langle \Delta y \rangle}{\Delta \tau} + [dD(y)/dy]\,, \tag{9.18}$$

The equation of evolution then becomes:

$$\frac{\partial p(y;t)}{\partial t} = \frac{\partial}{\partial y}\, [F(y)\, p(y;t)] + \frac{\partial}{\partial y} \left[D(y)\, \frac{\partial}{\partial y} p(y;t) \right]\,. \tag{9.19}$$

We stress its analogy with the DIFFUSION EQUATION of macroscopic physics:

$$\frac{\partial n(y;t)}{\partial t} = D\, \frac{\partial^2 n(y;t)}{\partial y^2}\,, \tag{9.20}$$

This parabolic partial differential equation describes (for instance) the monotonous evolution of an initial density inhomogeneity towards a final equilibrium density profile (whose shape depends on the boundary conditions). It is a typical IRREVERSIBLE BEHAVIOUR, as can be seen by the lack of invariance of this process under time inversion $(t \rightarrow -t)$ [see Sec. 2.2]. The additional first-order term in the Fokker-Planck equation describes a systematic slowing down, called the *dynamical friction*.

Eq. (9.17) is a very important and celebrated equation due to EINSTEIN: it relates the diffusion coefficient to the ratio of the mean square displacement to the time step. This equation is very often used in order to obtain a first guess of the transport coefficients in complicated systems. It will be met again repeatedly in forthcoming chapters.

The Fokker-Planck equation looks very different from the Gain-Loss equation (9.12), although both are consequences of the Chapman-Kolmogorov equation (9.7). They both describe a Markovian stochastic process, with different additional assumptions. We now show that there exists a more direct relation between these two processes: the Fokker-Planck equation can be derived directly from the Gain-Loss equation, with an additional assumption. In order to prove this statement, we define a new set of variables (average and relative variables):

$$\tfrac{1}{2}\left(y + y'\right) = Y, \qquad y' - y = \eta. \tag{9.21}$$

We then express the transition probability per unit time as follows:

$$W_t(y' \mid y) = W(y + \tfrac{1}{2}\eta; \eta). \tag{9.22}$$

We now make the following assumptions:

a) The transition probability per unit time is independent of time;

b) The transition probability per unit time is an even function of η: $W(y + \tfrac{1}{2}\eta; \eta) = W(y - \tfrac{1}{2}\eta; -\eta)$;

c) On the average, the *jumps are small* compared to the initial values of y:[2]

$$\eta \ll y \tag{9.23}$$

Assumption b) means that the probabilities of the direct and inverse transitions are equal; assumption c) will be made more precise below. Under these assumptions, the Gain-Loss equation (9.12) is written as follows:

$$\partial_t p(y; t) = \int d\eta\, W(y + \tfrac{1}{2}\eta; \eta)\, \left[-p(y; t) + p(y + \eta; t)\right].$$

---

[2]This statement is picturesque, but not very accurate. In a stochastic process, jumps of all sizes η are possible at any given time. It may, however, be required that small jumps are much more probable than large ones. This will be expressed below as assumption c').

The functions $W(y + \frac{1}{2}\eta; \eta)$ and $p(y + \eta; t)$ are expanded under the condition (9.23) and the result is written, up to second order in η as:

$$\partial_t p(y; t) = \int d\eta \left\{ \eta W(y; \eta) \frac{\partial p(y; t)}{\partial y} + \frac{1}{2}\eta^2 \left[W(y; \eta) \frac{\partial^2 p(y; t)}{\partial y^2} + \frac{\partial W(y; \eta)}{\partial y} \frac{\partial p(y; t)}{\partial y} \right] \right\} + \dots$$

As $W(y; \eta)$ is an even function of η, the first term vanishes; in the second term we recognize the second order transition moment (9.15):

$$\int d\eta\, \eta^2\, W(y; \eta) = B(y) = 2D(y).$$

Assumption c) is now made more precise as follows:

c') The fourth transition moment (i.e., the average of η^4) is negligible compared to the second.

We then obtain:

$$\partial_t p(y; t) = \frac{\partial}{\partial y} D(y) \frac{\partial}{\partial y} p(y; t). \tag{9.24}$$

Thus, with our assumptions, *the Gain-Loss equation reduces to a Fokker-Planck equation* (with $F(y) = 0$). The basic feature which transformed the former integral equation into a differential equation is assumption c). The latter could seem rather artificial; it will appear, however, that many physical problems lead precisely to this type of process.

In this brief review we defined some important concepts of the theory of stochastic processes and derived two important equations of evolution: the Gain-Loss equation (9.12) and the Fokker-Planck equation (9.19). They have two properties in common:

α) They are *linear equations* of evolution for the probability density of a random variable;

β) They describe an *irreversible process* of approach to equilibrium.

We do not develop here the methods of solution or the possible generalizations of these equations: a vast literature is available on the subject. We rather return to the analysis of the kinetic equations.

9.3 Nature of the Collision Process

In order to further analyze the concept of a kinetic equation, we discuss the various types of collision terms obtained in the previous equations. We wish to underline their links with the stochastic concepts discussed above, as well as their mutual interrelations. We begin our discussion with the Boltzmann equation for a dilute gas, for reasons that will become obvious. For simplicity, we analyze here the problem of homogeneous systems, postponing the discussion of inhomogeneous systems to forthcoming sections.

The Boltzmann equation

We rewrite the Boltzmann equation (7.44) in a slightly different form, introducing the notation $g\sigma = W(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2)$:

$$\partial_t \varphi(\mathbf{v}_1; t) = n \int d\mathbf{v}_2 \, d\Omega \, W(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) \, \{\varphi(\mathbf{v}'_1; t) \, \varphi(\mathbf{v}'_2; t) - \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t)\} \, .$$

$$(9.25)$$

This equation has a typical *probabilistic form* of a *Gain-Loss process*, of the type described in Sec. 9.2, Eq. (9.12). The second term describes the transition of a couple of particles $(1, 2)$ from an initial "state" where they had velocities $\mathbf{v}_1$, $\mathbf{v}_2$ to a final "state" where they have different velocities $\mathbf{v}'_1$, $\mathbf{v}'_2$. The probability density of particles at point $\mathbf{v}_1$ decreases during this process: hence a negative contribution to $\partial_t \varphi(\mathbf{v}_1; t)$. The first term represents the inverse transition, from the "state" $\mathbf{v}'_1$, $\mathbf{v}'_2$ to the "state" $\mathbf{v}_1$, $\mathbf{v}_2$: this produces a positive contribution to $\partial_t \varphi(\mathbf{v}_1; t)$. Both processes have the same transition probability density per unit time, proportional to $W(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2)$. The total rate of change of $\varphi(\mathbf{v}_1; t)$ is obtained by summing over all velocities $\mathbf{v}_2$ of the collision partner 2 and over all values of the solid angle Ω characterizing the final velocities. Momentum and energy are conserved in the collision process [see (7.35)].

The evolution process thus apepars as a sequence of transitions from a well-defined initial state to another well-defined final state: nothing is said about what happens *during* the interaction in the region where the particles are close enough to feel each other's influence. After the interaction, the particles "start a new life": they are in no way influenced by their past history. Something can also be said about the future: two specific ("tagged") particles having once collided, will never recollide (see also Sec. 6.2). Indeed, after a collision each particle moves along a very complicated path that is constantly perturbed by collisions with other particles; a recollision of the *same* two particles at a later time would be a "miracle"! This discussion requires, clearly, that the system has very many particles, with a finite local density. In other words, it implies the thermodynamic limit [assumption A)].

The evolution is described as a MARKOVIAN STOCHASTIC PROCESS. This picture of the particle motion is, of course, at variance with the deterministic description of classical mechanics, in which the Hamiltonian and the initial conditions determine every detail of the orbit, even within the effective interaction region: there seems to be no place for probability here.

In Boltzmann's time, the mathematical techniques of statistical mechanics were, of course, not sufficiently developed in order to allow a rigourous derivation of a kinetic equation from first principles. It is therefore remarkable that, combining the laws of dynamics with a scientific intuition that bears the sign of genius, Boltzmann was able to obtain an equation that survived unchanged all the great revolutions of the

physics of the beginning of the 20-th century. His original derivation was based on the picture described above. The collisions were considered as random instantaneous transitions during which some particles are lost in a neighbourhood of the point **v** in phase space, whereas other particles enter this region.

Boltzmann's equation was not easily accepted by his contemporaries. The objections that were opposed to his work were all addressed to his having "dared" to introduce the concept of probability into a science that was supposed to be the paradigm of a perfectly deterministic theory. In particular, his way of counting the collisions (*"Stosszahlansatz"*) as completed, uncorrelated events was criticized by Boltzmann's contemporaries. We shall not discuss here these objections in detail: they posed the very deep problem of the compatibility of irreversible evolution with the laws of mechanics. They therefore contested the fact that Boltzmann's remarkable success in explaining the entropy and the second law of thermodynamics (see Sec. 9.4) was really derived from mechanics. After a period of very heated controversy, the problem of the foundation of the Boltzmann equation was abandoned (because of lack of a good theory of many-body systems) around 1910. The practical consequences of the kinetic equation were, however, developed into an efficient technique which proved quite successful in obtaining transport coefficients that compared very well with the experimental values. It was only around 1945-1960 that the progress of the mathematical techniques developed in quantum field theory strongly influenced nonequilibrium statistical mechanics and led to an important reformulation of this science. The works of N.N. Bogolioubov, L. Van Hove, I. Prigogine and his coworkers were crucial in leading to a general methodology for really *deriving* kinetic equations from classical or quantum mechanics. Some of the basic problems are, however, not completely understood and are still the object of active research.

In the modern derivation presented here, the Markovian form of the kinetic equation results from an *asymptotic treatment* of the exact dynamical equations, combined with the assumptions A) - D) of Sec. 9.1. This argument leads to two different ways of formulating the conclusion. On one hand, it may be stated that there are no Markovian processes in nature. If all the fine details of the motion are retained, one sees no sudden jump from **v** to **v'** during a collision, but rather a continuous bending of the orbit, whose shape is determined by the past history, down to the initial condition. On the other hand, whenever the unobservable details of the orbit are smoothed out (over the time scale $\tau_R \gg \tau_C$) the evolution process looks *as if* it were Markovian.

A difference with the elementary stochastic Gain-Loss process (9.12) should be stressed. Boltzmann's kinetic equation is a *nonlinear equation*: the nonlinearity introduces, as always, essentially new properties and a wealth of solutions that have no equivalent in a linear version.

In conclusion, we now define a COLLISION as *a process of transition of a group of*

particles from an initial state to a final state having the same total momentum and energy; this process is **completed** *during a negligibly short time* τ_C *and in a region of negligibly small size* l_C. Thus, a collision is considered as a quasi-instantaneous and quasi-pointlike event. As a result, the evolution is no longer described as a dynamical process (i.e., a continuous unfolding of a canonical transformation generated by a Hamiltonian) but rather as a succession of separate transitions characterized by a transition *probability*. This new feature introduces an essential difference between the description of the evolution in ordinary dynamics and in statistical dynamics. It should be stressed, however, that the kinetic equation was *derived* from exact dynamics within a framework of well-defined conditions of validity.

The Landau Equation

At first sight, the Landau equation for a homogeneous system [obtained from (6.26)] is very different from the Boltzmann equation:

$$\partial_t \varphi(\mathbf{v}_1; t) = \frac{8\pi^4 n}{m^2} \int d\mathbf{v}_2 \int d\mathbf{k} \, \tilde{V}^2(k) \, (\mathbf{k} \cdot \partial_{12}) \, \delta(\mathbf{k} \cdot \mathbf{g}) \, (\mathbf{k} \cdot \partial_{12}) \, \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_1; t).$$

(9.26)

Instead of a Gain-Loss equation we find a partial differential operator, suggesting something rather similar to a diffusion-like process. We now show that this difference, though important, is not essential. It was actually seen in the previous section that a differential equation (the Fokker-Planck equation) can be derived from a Gain-Loss equation under some special assumptions. A similar argument can be applied to the *nonlinear* Boltzmann equation: the calculation given below is precisely the original derivation of Landau, in 1936.

From Eq. (7.35) we obtain:

$$\mathbf{v}_1' = \mathbf{v}_1 + \boldsymbol{\Delta}, \qquad \mathbf{v}_2' = \mathbf{v}_2 - \boldsymbol{\Delta}, \tag{9.27}$$

where the velocity deviation is:

$$\boldsymbol{\Delta} = -\tfrac{1}{2}(\mathbf{g} - g\mathbf{e}). \tag{9.28}$$

The collision probability density per unit time is expressed in terms of new variables as follows:

$$
\begin{aligned}
W(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2') \quad &\rightarrow \quad W[\tfrac{1}{2}(\mathbf{v}_1 + \mathbf{v}_1'), \tfrac{1}{2}(\mathbf{v}_2 + \mathbf{v}_2'); \mathbf{v}_1' - \mathbf{v}_1, \mathbf{v}_2' - \mathbf{v}_2] \\
&= \quad W(\mathbf{v}_1 + \tfrac{1}{2}\boldsymbol{\Delta}, \mathbf{v}_2 - \tfrac{1}{2}\boldsymbol{\Delta}; \boldsymbol{\Delta}, -\boldsymbol{\Delta}) \\
&\equiv \quad W(\mathbf{v}_1 + \tfrac{1}{2}\boldsymbol{\Delta}, \mathbf{v}_2 - \tfrac{1}{2}\boldsymbol{\Delta}; \boldsymbol{\Delta})
\end{aligned}
$$

(9.29)

Direct and inverse collisions have the same probability, hence the property:

$$W(\mathbf{v}_1 + \tfrac{1}{2}\boldsymbol{\Delta}, \mathbf{v}_2 - \tfrac{1}{2}\boldsymbol{\Delta}; \boldsymbol{\Delta}) = W(\mathbf{v}_1 + \tfrac{1}{2}\boldsymbol{\Delta}, \mathbf{v}_2 - \tfrac{1}{2}\boldsymbol{\Delta}; -\boldsymbol{\Delta}). \tag{9.30}$$

The Boltzmann equation takes the following form in the new variables:

$$\begin{aligned}
\partial_t \varphi(\mathbf{v}_1; t) &= n \int d\mathbf{v}_2 \, d\Omega \, W(\mathbf{v}_1 + \tfrac{1}{2}\boldsymbol{\Delta}, \mathbf{v}_2 - \tfrac{1}{2}\boldsymbol{\Delta}; \boldsymbol{\Delta}) \\
&\quad \times \{ \varphi(\mathbf{v}_1 + \boldsymbol{\Delta}; t) \, \varphi(\mathbf{v}_2 - \boldsymbol{\Delta}; t) - \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t) \}.
\end{aligned} \tag{9.31}$$

We now assume that the deviation resulting from a collision is small (on the average) compared to the initial velocities:

$$\boldsymbol{\Delta} \ll \mathbf{v}_i, \quad i = 1, 2 \tag{9.32}$$

Performing an expansion analogous to the one done in Eq. (??) we find:

$$\begin{aligned}
\partial_t \varphi(\mathbf{v}_1; t) &= n \int d\mathbf{v}_2 \, d\Omega \, \{ \Delta^r \, W(\mathbf{v}_1, \mathbf{v}_2; \boldsymbol{\Delta}) \, \partial_{12}^r \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t) \\
&\quad + \tfrac{1}{2} \Delta^r \Delta^s \, [W(\mathbf{v}_1, \mathbf{v}_2; \boldsymbol{\Delta}) \, \partial_{12}^r \partial_{12}^s \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t) \\
&\quad + (\partial_{12}^r W(\mathbf{v}_1, \mathbf{v}_2; \boldsymbol{\Delta})) \, \partial_{12}^s \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t)] \}
\end{aligned}$$

The first term vanishes because of (9.30), and after some elementary algebra, the result is put into the form:

$$\partial_t \varphi(\mathbf{v}_1; t) = \frac{n}{m^2} \int d\mathbf{v}_2 \, \partial_{12}^r \, G^{rs} \, \partial_{12}^s \, \varphi(\mathbf{v}_1; t) \, \varphi(\mathbf{v}_2; t), \tag{9.33}$$

with:

$$G^{rs} = \frac{m^2}{2} \int d\Omega \, \Delta^r \Delta^s \, W(\mathbf{v}_1, \mathbf{v}_2; \boldsymbol{\Delta}) . \tag{9.34}$$

We thus recovered an equation of the form (6.22): it only remains to be shown that the tensor G^{rs} is identical in the two equations.

The change of momentum $m\boldsymbol{\Delta}$ of the first particle can be expressed as the time integral of the force due to the second particle, taken along the whole orbit of the collision (this means that a *collision* is again considered as a closed, completed process!):

$$m\boldsymbol{\Delta} = - \int_{-\infty}^{\infty} dt \, \frac{\partial V \left[\mathbf{q}_1(t) - \mathbf{q}_2(t) \right]}{\partial \mathbf{q}_1}, \tag{9.35}$$

where the instantaneous distance is expressed in terms of the distance **a** at some arbitrary initial time as:

$$\mathbf{r}(t) \equiv \mathbf{q}_1(t) - \mathbf{q}_2(t) = \mathbf{a} + \int_0^t ds\, \mathbf{g}(s).$$

We now introduce the assumption of *weak coupling*. The time dependence of the relative velocity $\mathbf{g}(s)$ is due to the accelerating action of the force; but Δ in Eq. (9.35) is already proportional to the force. Hence, to first approximation in the strength of the force, we replace $\mathbf{g}(s)$ by a constant $\mathbf{g}$, and:

$$\mathbf{r}(t) \approx \mathbf{a} + \mathbf{g}\, t.$$

This amounts to replacing the slightly bent trajectory of a particle by its straight asymptote (Fig. 9.1). Introducing this approximation into (9.35) and going over to the Fourier representation, we find

$$m\Delta = -\int_{-\infty}^{\infty} dt \int d\mathbf{k}\, i\mathbf{k}\, \tilde{V}(k)\, e^{i\mathbf{k}\cdot(\mathbf{a}+\mathbf{g}t)}. \tag{9.36}$$

In Fig. 9.1 we introduce a reference frame whose origin is at $\mathbf{q}_1$ and whose z-axis is directed along the relative velocity $\mathbf{g}$. The orbit of particle 1 meets the $x-y$ plane at the point of closest approach, i.e. (approximately) at a distance b from the origin, and its position vector makes an angle ϕ with the x-axis.
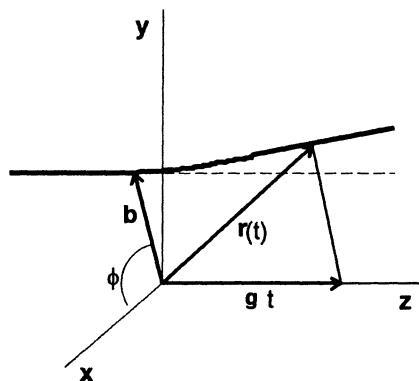

Figure 9.1: Collision geometry in a weakly coupled system.

We then note, comparing (7.44) and (7.34):

$$W(\mathbf{v}_1, \mathbf{v}_2; \Delta)\, d\Omega = g\sigma\, d\Omega = gb\, d\phi\, db,$$

hence (9.34) can be rewritten as:

$$
\begin{aligned}
G^{rs} = {} & \frac{1}{2} \int_0^\infty db \int_0^{2\pi} d\phi\, bg \int_{-\infty}^\infty dt_1 \int_{-\infty}^\infty dt_2 \int d\mathbf{k}_1 \int d\mathbf{k}_2 \\
& \times i k_1^r\, i k_2^s\, \tilde{V}(k_1)\, \tilde{V}(k_2)\, \exp\left[i\mathbf{k}_1 \cdot \mathbf{r}(t_1) + i\mathbf{k} \cdot \mathbf{r}(t_2)\right]
\end{aligned}
\tag{9.37}
$$

One finally notes that in the reference frame of Fig. 9.1 the vector $\mathbf{r}(t_1)$ has cylindrical coordinates (b, ϕ, gt_1), hence:

$$
\int_0^\infty db\, b \int_0^{2\pi} d\phi \int_{-\infty}^\infty dt_1\, g = \int d\mathbf{r}(t_1).
$$

Using all these results, Eq. (9.37) is brought to the form:

$$
\begin{aligned}
G^{rs} = {} & \frac{1}{2} \int d\mathbf{r} \int d\tau \int d\mathbf{k}_1 d\mathbf{k}_2 \\
& \times i k_1^r\, i k_2^s\, \tilde{V}(k_1)\, \tilde{V}(k_2)\, \exp\left[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r} + i\mathbf{k}_2 \cdot \mathbf{g}\tau\right].
\end{aligned}
$$

The integrations are now elementary, and we recover exactly the expression (6.22).

The physical content of the Boltzmann and of the Landau equations is thus the same, and their apparent difference is easily understood. In the former case, the strong interaction potential can produce a finite, arbitrarily large momentum transfer during a collision. As a result, the difference between the initial and the final state of the completed collision is a finite quantity, as seen in the curly bracketted terms of Eq. (9.25). In the Landau case, however, a very weak interaction potential necessarily produces an infinitesimal change of the momenta of the collision partners, as seen in Eq. (9.35). Hence, Eq. (9.26) describes the effect of a completed collision, just as (9.25); because of the weak coupling, the Gain-Loss difference appears as a second derivative of the RDF's with respect to the velocity.

The Landau collision term can be written in the following general form:[3]

$$
\partial_t \varphi(\mathbf{v}_1; t) = \partial_1 \cdot \mathsf{D}(\mathbf{v}_1; t) \cdot \partial_1 \varphi(\mathbf{v}_1; t) + \partial_1 \cdot \mathbf{F}(\mathbf{v}_1; t)\, \varphi(\mathbf{v}_1; t).
\tag{9.38}
$$

We do not write down explicitly the tensor $\mathsf{D}(\mathbf{v}_1; t)$ and the vector $\mathbf{F}(\mathbf{v}_1; t)$ which are easily obtained from Eq. (9.26). Eq. (9.38) resembles the *Fokker-Planck equation* (9.19), but is not identical to it. Besides the trivial fact that (9.38) is relative to a three-dimensional random variable $\mathbf{v}$, the most important difference is its *nonlinear*

---

[3]We note that the first operator $\partial_{12} = \partial_1 - \partial_2$ in the integrand of Eq. (9.26) can be replaced by ∂_1: indeed, the second term ∂_2 gives a vanishing contribution to the integral, because of Eq. (4.26). We shall sometimes keep the expression ∂_{12} as such, for reasons of symmetry.

character[4]: both $D(\mathbf{v}_1; t)$ and $\mathbf{F}(\mathbf{v}_1; t)$ are functionals of the RDF $\varphi(\mathbf{v}_1; t)$. In spite of its form, the Landau equation cannot qualify as a (generalized) Fokker-Planck equation for the same reasons that the Vlasov equation (5.23) is not a Liouville equation for a system in an external field. The "diffusion tensor" $D(\mathbf{v}_1; t)$ and the "dynamical friction" $\mathbf{F}(\mathbf{v}_1; t)$ are self-consistent quantities, that adjusts themselves to the instantaneous value of $\varphi(\mathbf{v}_1; t)$ as time passes. For all these reasons, the name "Fokker-Planck equation", often given to Eq. (9.26) in the literature should be avoided in favour of the correct name of Landau equation, which designates a different type of evolution mechanism.

In spite of these remarks, Eq. (9.38) possesses a *diffusive character* that is one of its most important properties. It is due to the presence of the second derivatives with respect to velocity: this is a completely new feature as compared to the Liouville or the BBGKY equations. It is the origin of an essential property: *the Landau equation describes an* IRREVERSIBLE PROCESS. This can be quickly seen by performing a *time inversion* transformation (see Sec.2.2). Upon changing $t \rightarrow -t$ and $\mathbf{v} \rightarrow -\mathbf{v}$, the left hand side changes sign, whereas the right hand side does not: the equation is NOT invariant under time inversion. This argument is not very rigourous, and should only be considered as indicative. We discuss this question in depth in Sec. 9.4

The Balescu-Lenard Equation

The whole discussion of the properties of the Landau equation applies as well to the Balescu-Lenard equation for plasmas. Indeed, Eq. (8.38) has the same form as the Landau equation; its interpreation in terms of collisions is thus the same as above. The interaction potential is, however, the self-consistently screened effective potential, including the dielectric constant. The equation is thus much more strongly nonlinear, but this does not affect its physical interpretation.

9.4   Irreversibility and Entropy

The crucial property of the kinetic equations in connection with the concept of irreversibility is a celebrated theorem derived by Boltzmann in 1872 as a property of his kinetic equation for dilute gases and which has kept its original name in a generalized sense. Before discussing its deeper meaning, we prove the theorem, for a spatially homogeneous system, for the three kinetic equations derived in Chaps. 6 - 8.

Boltzmann's H-theorem.

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[4]It should be noted that Eq. (9.38) is much more strongly nonlinear than the object called as such in the traditional terminology. In his classical book, van Kampen gives the name "nonlinear Fokker-Planck equation" to any equation of the form (9.38), in which $D(\mathbf{v})$ and $\mathbf{F}(\mathbf{v})$ are functions of the velocity, but NOT of the unknown function $\varphi(\mathbf{v}; t)$.

Consider a weakly coupled, spatially homogeneous system, whose RDF $\varphi(\mathbf{v};t)$ obeys either one of the following kinetic equations:

  *a) the **Boltzmann equation** (9.25),*
  *b) the **Landau equation** (9.26),*
  *c) the **Balescu-Lenard equation** (8.38).*

  There exists a functional $s(t)$ of the RDF,[5] depending on time only through $\varphi(\mathbf{v};t)$; $s(t)$ is a monotonously increasing function of time for all RDF's defined above:

$$\frac{ds(t)}{dt} \geq 0 \,. \tag{9.39}$$

Boltzmann equation.

The functional $s(t)$ is defined as follows:

$$s(t) = -k_B \int d\mathbf{v} \, \ln\left[n\varphi\left(\mathbf{v};t\right)\right] \varphi(\mathbf{v};t) + b \,, \tag{9.40}$$

where $k_B > 0$ and b are constants, that will be determined afterwards. The time derivative of this functional is obtained as follows, by using the kinetic equation:

$$
\begin{aligned}
d_t s(t) &= -k_B \int d\mathbf{v}_1 \left\{\ln\left[n\varphi\left(\mathbf{v}_1;t\right)\right] + 1\right\} \partial_t \varphi(\mathbf{v}_1;t) \\
&= -2\pi k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \left[\ln n\varphi(\mathbf{v}_1;t) + 1\right] \\
&\qquad \times \left\{\varphi(\mathbf{v}_1';t)\varphi(\mathbf{v}_2';t) - \varphi(\mathbf{v}_1;t)\varphi(\mathbf{v}_2;t)\right\} \\
&= -2\pi k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \left[\ln n\varphi(\mathbf{v}_2;t) + 1\right] \{...\} \\
&= -\pi k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \left[\ln n\varphi(\mathbf{v}_1;t) + \ln n\varphi(\mathbf{v}_2;t) + 2\right] \{...\} \\
&= +\pi k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \left[\ln n\varphi(\mathbf{v}_1';t) + \ln n\varphi(\mathbf{v}_2';t) + 2\right] \{...\} \\
&= \tfrac{1}{2}\pi k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \ln \frac{\varphi(\mathbf{v}_1';t)\varphi(\mathbf{v}_2';t)}{\varphi(\mathbf{v}_1;t)\varphi(\mathbf{v}_2;t)} \\
&\qquad \times \left\{\varphi(\mathbf{v}_1';t)\varphi(\mathbf{v}_2';t) - \varphi(\mathbf{v}_1;t)\varphi(\mathbf{v}_2;t)\right\} \geq 0 \,. \tag{9.41}
\end{aligned}
$$

We first noted that the dummy integration variables $\mathbf{v}_1, \mathbf{v}_2$ may be interchanged: in this process $\mathbf{v}_1' \to \mathbf{v}_2'$, $\mathbf{v}_2' \to \mathbf{v}_1'$, $\mathbf{g} \to -\mathbf{g}$. The original expression is then replaced by the half-sum of the two equal quantities. Next, we note that we may replace under the integral $\mathbf{v}_1 \to \mathbf{v}_1'$, $\mathbf{v}_2 \to \mathbf{v}_2'$. The final symmetrization leads to the expression in the

---

[5]Boltzmann used the notation $H(t) = -s(t)$, whence the name of the theorem.

last side of the equality. This last expression is nonnegative, because of the following identity that holds, whatever the values of x and y, provided they are positive:[6]

$$(x - y) \ln \left(\frac{x}{y} \right) \geq 0. \tag{9.42}$$

The H-theorem is thus proved.

The Landau equation

The basic functional is again defined by Eq. (9.40), and we calculate its time derivative by using the kinetic equation (9.26) which governs the evolution of $\varphi(\mathbf{v}; t)$. [For compactness in the forthcoming proofs, we abbreviate $\varphi(\mathbf{v}_k; t)$ by $\varphi(k)$; we also use: $A = 8\pi^4 m^{-2}$].

$$
\begin{aligned}
d_t s(t) &= -k_B \int d\mathbf{v}_1 \left[\ln n\varphi(1) + 1 \right] \partial_t \varphi(1) \\
&= -A k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{k} \left[\ln n\varphi(1) + 1 \right] \tilde{V}^2(k) \, \mathbf{k} \cdot \partial_{12} \delta(\mathbf{k} \cdot \mathbf{g}) \, \mathbf{k} \cdot \partial_{12} \varphi(1) \varphi(2) \\
&= -A k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{k} \left[\ln n\varphi(2) + 1 \right] \tilde{V}^2(k) \, \mathbf{k} \cdot \partial_{12} \delta(\mathbf{k} \cdot \mathbf{g}) \, \mathbf{k} \cdot \partial_{12} \varphi(1) \varphi(2) \\
&= -\tfrac{1}{2} A k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{k} \left[\ln n\varphi(1) + \ln n\varphi(2) + 2 \right] \tilde{V}^2(k) \, \mathbf{k} \cdot \partial_{12} \delta(\mathbf{k} \cdot \mathbf{g}) \, \mathbf{k} \cdot \partial_{12} \varphi(1) \varphi(2) \\
&= +\tfrac{1}{2} A k_B n \int d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{k} \left[\varphi(1) \, \varphi(2) \right]^{-1} \tilde{V}^2(k) \, \delta(\mathbf{k} \cdot \mathbf{g}) \, \left[\mathbf{k} \cdot \partial_{12} \varphi(1) \varphi(2) \right]^2 \geq 0. \tag{9.43}
\end{aligned}
$$

In going from the second to the third step we made use of the symmetry of the integrand ($\mathbf{v}_1$ and $\mathbf{v}_2$ are dummy integration variables). The fourth step represents the half-sum of two equal expressions. In the last step we performed an integration by parts. Clearly, the integrand in the last expression is positive definite: the probability distributions $\varphi(k)$ as well as the delta-function are nonnegative, and the other factors under the integral are squares. Eq. (9.39) is thus proved.

The Balescu-Lenard equation

The proof of the H-theorem for Eq. (8.38) is exactly identical to the case of the Landau equation; one simply replaces $\tilde{V}^2(k)$ by $\tilde{V}^2(k)/\left| \varepsilon(\nu) \right|^2$.
We have thus proved the H-theorem for all three kinetic equations.

The function $s(t)$ is thus a monotonously increasing function of time. Two possibilities exist for its behaviour as $t \to \infty$: either $s(t) \to \infty$, (Fig. 9.2, A) or $s(t)$ is bounded above, i.e., it tends monotonously toward a finite value (Fig. 9.2, B).

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[6] If $x > y$, $(x/y) > 1$ and $\ln(x/y) > 0$; when $x < y$, $(x/y) < 1$ and $\ln(x/y) < 0$.
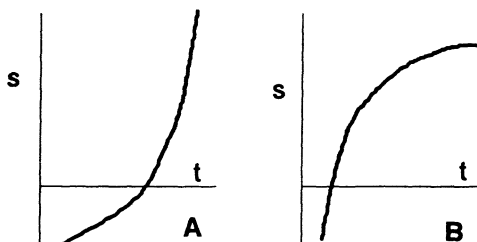
Figure 9.2: Two possible shapes for the curve $s(t)$.

It is easily shown that under a reasonable condition, the latter case is realized. We assume that the average kinetic energy is a finite quantity; this implies:

$$\int d\mathbf{v}\, v^2 \varphi(\mathbf{v}; t) < \infty\,. \tag{9.44}$$

We know that, as $v \to \infty$, $\varphi(\mathbf{v}; t) \to 0$, hence $\ln\varphi(\mathbf{v}; t) \to -\infty$. The question arises: how fast does $\ln\varphi(\mathbf{v}; t)$ go to $-\infty$? If it decreases slower than v^2, the integral (9.40) converges, because of (9.44). A divergence could only appear if $[-\ln\varphi(\mathbf{v}; t)]$ tends to infinity faster than v^2; but in this case $\varphi(\mathbf{v}; t)$ decreases faster than $\exp(-v^2)$, which dominates the factor $[-\ln\varphi(\mathbf{v}; t)]$ and makes the integral of $\varphi(\mathbf{v}; t)\ln\varphi(\mathbf{v}; t)$ convergent.

The first important consequence of the H-theorem can be formulated as follows. *Whatever the initial condition, the RDF $\varphi(\mathbf{v}; t)$ evolves in time in such a way that the functional $s(t)$ increases monotonously.* The function $s(t)$ thus provides an *arrow of time.* Any evolution that would lead to a decrease of $s(t)$, even for a limited time (such as an oscillation), is excluded by the H-theorem. This also implies that when the system evolves from time t_1 to t_2 with an increase of $s(t)$, the "reverse" motion that would imply a corresponding decrease of $s(t)$ is impossible. The H-theorem thus gives a precise meaning to the concept of IRREVERSIBILITY associated with the kinetic equations.

A second consequence of the H-theorem is: *Whatever the initial condition, the evolution reaches a final point, i.e., a stationary state, when $s(t)$ reaches its maximum value (which is finite).* It is important to identify the form of the RDF in this final, stationary state.

Boltzmann equation

It is easily seen that the final stationary solution is the *Maxwell distribution:*

$$\varphi^0(\mathbf{v}) = c \exp\left[-a \left|\mathbf{v} - \mathbf{u}\right|^2\right],\tag{9.45}$$

where the scalars c, a and the vector $\mathbf{u}$ are arbitrary constants. Indeed, for a solution to be stationary, Eq. (9.41) requires:

$$\varphi^0(\mathbf{v}_1')\varphi^0(\mathbf{v}_2') = \varphi^0(\mathbf{v}_1)\varphi^0(\mathbf{v}_2)$$

or:

$$\ln \varphi^0(\mathbf{v}_1') + \ln \varphi^0(\mathbf{v}_2') = \ln \varphi^0(\mathbf{v}_1) + \ln \varphi^0(\mathbf{v}_2).$$

Substituting (9.45) and using (7.37) we obtain:

$$
\begin{aligned}
&-a\left(\mathbf{v}_1' - \mathbf{u}\right)^2 - a\left(\mathbf{v}_2' - \mathbf{u}\right)^2\\
=\ &-a\tfrac{1}{4}\left(\mathbf{v}_1 + \mathbf{v}_2 + |\mathbf{v}_1 - \mathbf{v}_2|\mathbf{e} - 2\mathbf{u}\right)^2 - a\tfrac{1}{4}\left(\mathbf{v}_1 + \mathbf{v}_2 - |\mathbf{v}_1 - \mathbf{v}_2|\mathbf{e} - 2\mathbf{u}\right)^2\\
=\ &-a\left(\mathbf{v}_1 - \mathbf{u}\right)^2 - a\left(\mathbf{v}_2 - \mathbf{u}\right)^2,
\end{aligned}
$$

an identity that is easily checked.

Landau and Balescu-Lenard equations

The Maxwell distribution (9.45) is also the stationary solution of the Landau and of the Balescu-Lenard equations. We note, indeed, that:

$$\mathbf{k} \cdot \partial_{12}\, \varphi^0(\mathbf{v}_1)\varphi^0(\mathbf{v}_2) = -2a\left(\mathbf{k} \cdot \mathbf{g}\right)\varphi^0(\mathbf{v}_1)\varphi^0(\mathbf{v}_2)\tag{9.46}$$

Substituting this result into the last integral of Eq. (9.43) we find an expression of the form $(\mathbf{k} \cdot \mathbf{g})^2\,\delta(\mathbf{k} \cdot \mathbf{g})$ which is identically zero.

It can be shown, moreover, that $\varphi^0(\mathbf{v})$ given by Eq. (9.45) is the only stationary solution of our kinetic equations. We also note that the constant vector $\mathbf{u}$ is not really significant in Eq. (9.45): it can always be eliminated by choosing a reference frame moving with the constant velocity $(-\mathbf{u})$ (a Galilei transformation that leaves the classical laws of motion invariant). We may thus take for the general stationary solution of the Landau equation the MAXWELL RDF *(or maxwellian distribution)*:

$$\varphi^0(\mathbf{v}) = c \exp(-a\, v^2).\tag{9.47}$$

This function only depends on the absolute value of the velocity and on two arbitrary constants a and c that will be presently identified.

Our conclusion after this analysis is that $s(t)$ is a monotonously growing function of time that tends to a finite maximum value as $t \to \infty$; in this final state the evolution stops, and the RDF reaches a stationary state, whose form is independent (up to two constants) of the initial distribution function. The stationary solution of the kinetic equation is the Maxwell distribution in the classical case. In other words, this is the *thermal equilibrium reduced distribution function* that is obtained in Equilibrium Statistical Mechanics by a completely different method (from the construction of the canonical ensemble).[7] This allows us to identify the arbitrary constants in Eqs. (9.45) and (9.47) in terms of the temperature T and the Boltzmann constant k_B. Indeed, from the canonical phase space distribution function (3.27), the one-particle reduced distribution function is easily calculated; one finds (even in presence of interactions!):

$$f^0(\mathbf{q}, \mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m}{2 k_B T} v^2 \right) . \qquad (9.48)$$

[Note that the equilibrium one-particle RDF is necessarily homogeneous]. Comparing this form with (9.47) we find the following values ensuring the consistency of equilibrium and non-equilibrium theories:

$$a = \frac{m}{2 k_B T} , \quad c = \left(\frac{m}{2\pi k_B T} \right)^{3/2} . \qquad (9.49)$$

We now recall that in macroscopic thermodynamics there exists a function of state which has the property of increasing monotonously during any spontaneous evolution of a system, and which reaches a maximum value in thermal equilibrium. This is the ENTROPY, whose properties are postulated by the celebrated Second Law of thermodynamics. The functional $s(t)$ of Boltzmann's H-theorem thus possesses all the specific attributes of the entropy (per particle). The correspondence is completed by fixing the following value for the constant b in Eq. (9.40):

$$b = k_B \ln \left(\frac{e}{h^3} \right) , \qquad (9.50)$$

(where e is the basis of the natural logarithms). One then finds, by evaluating Eq. (9.40) with the Maxwellian equilibrium distribution (9.48) the following result for the entropy *density*:

$$ns(\infty) = n k_B \left[-\ln n + \tfrac{5}{2} + \tfrac{3}{2} \ln \left(2\pi m k_B T h^{-2} \right) \right] . \qquad (9.51)$$

We recall that in equilibrium statistical mechanics, the thermodynamic properties are derived from the canonical equilibrium ensemble via the partition function

---

[7]It is important to note that the delta-function expressing energy conservation is essential for ensuring that the equilibrium solutions are indeed stationary solutions of the kinetic equations. This delta-function originates from the asymptotic theory, i.e., Assumption E).

$Z(T, V, N)$, Eq. (3.28). The connection with thermodynamics is obtained via the basic formula for the Helmholtz free energy $A(T, V, N)$, Eq. (3.29). The entropy density is then obtained by the thermodynamic formula (3.31), from which we derive:

$$ns = -\frac{1}{V} \left(\frac{\partial A}{\partial T} \right)_{V,N} .$$ \hfill (9.52)

Upon evaluating the entropy density for a classical ideal system by the formalism of equilibrium statistical mechanics, one finds exactly the result (9.51).

It should be stressed at this point that the entropy, as defined by Eq. (9.40) is a typical *thermal quantity*, in the sense defined at the end of Sec. 3.2. It is NOT the average of a microscopic dynamical function; it would be meaningless to speak about the entropy of a single particle. Its definition could be formally interpreted as the "average" of the function $\ln f$, i.e. a functional of the entire instantaneous phase-space configuration of the system. Entropy thus appears as an essentially collective property.

We may now formulate the following fundamental conclusions, summarizing the results of this section.

- *The H-theorem implies that the kinetic equation describes an* IRREVERSIBLE EVO-LUTION *during which the RDF evolves monotonously [in such a way that $s(t)$ is increasing] towards the thermal equilibrium distribution; the latter is the end-point of the evolution, whatever the initial RDF. The motor of this evolution is provided by the collisions.*

- *The functional $ns(t)$ is identified with the thermodynamic entropy density.*

- *The H-theorem establishes the precise link between the dynamic, nonequilibrium statistical mechanics (i.e., the kinetic theory) and the static, equilibrium statistical mechanics.*

9.5   Spatially Inhomogeneous Systems

We have seen in the previous section that the *collisions* produce an irreversible evolution of the system towards equilibrium. For a clear discussion of this property, we considered a spatially homogeneous system, in which the collisions are the only cause of change in time. We now discuss the more general case of a spatially inhomogeneous system. In this case two additional mechanisms contribute to the dynamics: the free motion and the Vlasov term. These have quite different properties as compared to the collisions, hence inhomogeneous systems provide us with a richer set of motors of the evolution.

The equation of evolution, exhibiting free motion, Vlasov term and collision term is given by Eq. (6.19), which we rewrite here:

$$(\partial_t + \mathbf{v}_1 \cdot \nabla_1) \, f(\mathbf{q}_1, \mathbf{v}_1; t) = \mathcal{V}\{f\,f\} + \mathcal{K}\{f\,f\} \,, \tag{9.53}$$

with the Vlasov term $\mathcal{V}\{f\,f\}$ defined in Eq. (5.21) and $\mathcal{K}\{f\,f\}$ representing the Boltzmann, Landau or Balescu-Lenard collision term. Both terms $\mathcal{V}$ and $\mathcal{K}$ are quadratically nonlinear in the RDF; there is, however, a basic difference between them. In the collision term, both functions $f(\mathbf{q}_1, \mathbf{v}_1)\,f(\mathbf{q}_1, \mathbf{v}_2)$ are evaluated at the *same point* $\mathbf{q}_1$. This expresses the basic fact that *the collision is a localized process*: two point particles interact whenever their relative distance happens to be within the interaction range l_C of the potential. But our assumption (6.9) about the character- ~~istic length scales tells us that $l_C \ll l_H$. Thus, the exact positions of the collision~~ partners during the collision process are indistinguishable on the hydrodynamic length scale. This interpretation follows directly from the derivation given in Sec. 6.2. Thus, the collision process is an event taking place in a region of typical size l_C which, in the asymptotic treatment leading to the kinetic equation, shrinks to an infinitesimally small one.

The picture is different in the Vlasov term. Here the two RDF's are evaluated at the "actual" positions of the two interacting particles: $f(\mathbf{q}_1, \mathbf{v}_1)\,f(\mathbf{q}_2, \mathbf{v}_2)$, but the treatment of the second particle is quite different from its handling in the collision term: the corresponding RDF is averaged over the whole space. Thus, the interaction partner of particle 1 is "smeared out" into a continuous "jelly", a picture diametrically opposite to a localized collision. *The mean field description of the Vlasov term is completely delocalized.*

We gain insight into the various mechanisms of evolution by studying the rate of change of the *entropy density*, which is defined as follows for an inhomogeneous system:

$$n(\mathbf{x}, t)s(\mathbf{x}, t) = -k_B \int dv dq \, \delta(\mathbf{q} - \mathbf{x}) \, f(\mathbf{q}, \mathbf{v}; t) \, \ln f(\mathbf{q}, \mathbf{v}; t) + nb \,. \tag{9.54}$$

This is a straightforward generalization of Eq. (9.40); notice the delta-function $\delta(\mathbf{q} - \mathbf{x})$ which appears in all microscopic dynamical functions associated with local densities. The rate of change of the entropy density is given by a sum of three terms, corresponding to the free motion, T_f, the Vlasov term, T_V, and the collisions, T_K:

$$\partial_t n(\mathbf{x}, \mathbf{t})s(\mathbf{x}, t) = T_f + T_V + T_K \,. \tag{9.55}$$

The free motion term is evaluated as follows [we use the following notations: $\nabla_1 = \partial/\partial \mathbf{q}_1$, $\nabla = \partial/\partial \mathbf{x}$; $d1 = d\mathbf{q}_1 d\mathbf{v}_1$; $f(1) = f(\mathbf{q}_1, \mathbf{v}_1; t)$]:

$$T_f \;=\; k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, [\ln f(1) + 1] \, \mathbf{v}_1 \cdot \nabla_1 f(1)$$

$$\begin{aligned}
&= -k_B \int d1 \, [\nabla_1 \delta(\mathbf{q}_1 - \mathbf{x})] \, [\ln f(1) + 1] \, \mathbf{v}_1 f(1) - k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, \mathbf{v}_1 \cdot \nabla_1 f(1) \\
&= +k_B \nabla \cdot \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, [\ln f(1)] \, \mathbf{v}_1 f(1) - k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, \mathbf{v}_1 \cdot \nabla_1 f(1) \\
&\quad + k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, \mathbf{v}_1 \cdot \nabla_1 f(1) \\
&= \nabla \cdot k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, [\ln f(1)] \, \mathbf{v}_1 f(1) \equiv -\nabla \cdot \boldsymbol{\Phi}_S(\mathbf{x}; t). \quad (9.56)
\end{aligned}$$

In the first step we performed a partial integration over $\mathbf{q}_1$; next we separated the two pieces of the first term; in the first of these we used the identity: $\nabla_1 \delta(\mathbf{q}_1 - \mathbf{x}) = -\nabla \delta(\mathbf{q}_1 - \mathbf{x})$. In the second piece we performed again a partial integration: this produces a term which compensates the last one. The result has the canonical form of the divergence of a flux $\boldsymbol{\Phi}_S(\mathbf{x}; t)$.

Next, we consider the Vlasov term: performing again a partial integration, we find:

$$\begin{aligned}
T_V &= -k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, [\ln f(1) + 1] \, \nabla_1 \langle V(1) \rangle \cdot \partial_1 f(1) \\
&= k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, \nabla_1 \langle V(1) \rangle \, f(1) \frac{1}{f(1)} \cdot \partial_1 f(1) = 0. \quad (9.57)
\end{aligned}$$

This term vanishes because of the lemma (4.26). We thus obtained a very important result: *The Vlasov term produces no change of the entropy: it is a purely* REVERSIBLE *mechanism of evolution.* It is for this reason that the Vlasov equation without a collision term does not qualify as a *bona fide* kinetic equation.

The contribution of the collisions (denoted by $\sigma(\mathbf{x}; t) \equiv T_K$) is obtained from (9.41) or (9.43) by the substitution $n\varphi \to f$. Collecting these results we obtain:

$$\partial_t n(\mathbf{x}, t) s(\mathbf{x}; t) = -\nabla \cdot \boldsymbol{\Phi}_S(\mathbf{x}; t) + \sigma(\mathbf{x}; t). \quad (9.58)$$

This is the standard form of a macroscopic BALANCE EQUATION (see Sec. 2.2): it tells us that the rate of change of the entropy density equals minus the divergence of the entropy flux, plus an entropy source, defined as follows (for the Landau entropy source):

$$\boldsymbol{\Phi}_S(\mathbf{x}; t) = -k_B \int d1 \, \delta(\mathbf{q}_1 - \mathbf{x}) \, \mathbf{v}_1 \, [\ln f(1)] \, f(1), \quad (9.59)$$

$$\begin{aligned}
\sigma(\mathbf{x}; t) &= \frac{4\pi^4}{m^2} k_B \int d1 \, d2 \, \delta(\mathbf{q}_1 - \mathbf{x}) \delta(\mathbf{q}_2 - \mathbf{x}) \int d\mathbf{k} \, \tilde{V}^2(k) \\
&\quad \times \delta(\mathbf{k} \cdot \mathbf{g}) \, [f(1) f(2)]^{-1} \, [\mathbf{k} \cdot \partial_{12} f(1) f(2)]^2. \quad (9.60)
\end{aligned}$$

Eq. (9.58) has precisely the form of the macroscopic *entropy balance equation* that is the basis of nonequilibrium thermodynamics. Upon considering the rate of change

of the entropy contained in a finite volume element, the first term in the right hand side describes the variation of entropy due to exchanges with the external world (entry or exit of entropy), whereas the second term expresses the production (or destruction) of entropy inside the volume element. The fact that the source term is non-zero means that entropy is not a conserved quantity. But a stronger statement can be made:

$$\sigma(\mathbf{x}; t) \geq 0. \tag{9.61}$$

This is the expression of the SECOND LAW OF THERMODYNAMICS.

Summarizing this discussion, we arrive that the following conclusion. *The evolution of an inhomogeneous system is due to the superposition of two* REVERSIBLE PROCESSES: *the free flow process and the action of the* **Vlasov mean field**, *and an* IRREVERSIBLE PROCESS: *the collisions. In the long run the latter dominates and drives the system to equilibrium, with a corresponding increase of the entropy.*

Our discussion of the Vlasov term was done for a general case: it is particularly relevant for plasmas. Considering, however, our assumptions C) and D) of Sec. 9.1, we see that the Vlasov term is negligible under these conditions. It was shown in Sec. 5.3 [see Fig. 5.2] that the average potential is very small whenever $l_C/l_H \ll 1$. We thus neglect the Vlasov term in the forthcoming discussions; the kinetic equation then reduces to:

$$\partial_t f(\mathbf{q}_1, \mathbf{v}_1; t) = -\mathbf{v}_1 \cdot \nabla_1 f(\mathbf{q}_1, \mathbf{v}_1; t) + \mathcal{K}\{f f\}. \tag{9.62}$$

In the hydrodynamic regime under consideration, the evolution of the RDF is due to two competing actions: the free flow term and the collision term. It is important to note that the characteristic times attached to these two mechanisms are quite different. The free flow term represents a *slow process*, acting on the long time scale τ_H, whereas the collision term represents a *fast process*, acting on the short time scale τ_R. The competition between these two mechanisms produces a peculiar behaviour of the RDF, that will be presently discussed.

We know that if the free flow term were absent, the collision term would drive the system to a state described by a stationary solution of the collision term:

$$f^{LE}(\mathbf{q}, \mathbf{v}; t) = n(\mathbf{q}; t) \left(\frac{m}{2\pi k_B T(\mathbf{q}; t)} \right)^{3/2} \exp \left[-\frac{m}{2k_B T(\mathbf{q}; t)} \, |\mathbf{v} - \mathbf{u}(\mathbf{q}; t)|^2 \right]. \tag{9.63}$$

There is an important difference between this function and the solution (9.45) or (9.48) determined for a homogeneous system. The function f^{LE} annuls the collision term [see (9.46)] even when the density n, the average velocity $\mathbf{u}$ and the temperature T are arbitrary functions of the position $\mathbf{q}$ and of the time t. We also note that the average velocity $\mathbf{u}$ can no longer be eliminated by a Galilei transformation, because it is not constant.

The RDF $f^{LE}(\mathbf{q}, \mathbf{v};t)$ is called a LOCAL EQUILIBRIUM DISTRIBUTION. The name is somewhat ambiguous, because $f^{LE}(\mathbf{q}, \mathbf{v};t)$ is NOT a stationary equilibrium distribution. Indeed, the collision term is not alone in the kinetic equation; we must also take into account the free flow term. The evolution of the RDF can thus be described schematically as follows. Starting from an arbitrary initial state, the collision term drives the system *quickly* ($\sim \tau_R$) toward a state *close to* the local equilibrium (9.63); then the state *slowly* ($\sim \tau_H$) evolves toward the final, homogeneous equilibrium state (9.48). A more detailed study of the evolution of inhomogeneous systems is done in Chap. 10.

9.6   The Collisional Invariants

The forthcoming chapter is devoted to the justification of hydrodynamics from statistical dynamics: this implies the derivation of balance equations for averages of dynamical functions $b(\mathbf{q}, \mathbf{v}; \mathbf{x}, t)$. The general procedure for this derivation is similar to (though simpler than) the one leading to the entropy balance equation in the previous section (9.58): the two sides of Eq. (9.62) are multiplied by b and the result is integrated over $\mathbf{q}$ and $\mathbf{v}$. The contribution of the free flow term turns out to be very simple, whereas the contribution of the colision term is much more complicated. It is therefore remarkable that all kinetic equations have an important property. There exists a class of dynamical functions, called COLLISIONAL INVARIANTS, $\psi_n(\mathbf{q}, \mathbf{v})$, defined as follows: *the contribution of the collisions to the rate of change of the average of these functions is identically zero, for any state of the system.* This property of the collision term is expressed as follows [we use here again the abbreviations of Eq. (9.43)]:

$$\int d1\,\psi_n(1)\,\mathcal{K}\{f\,f\} = 0\,, \quad \forall f\,. \tag{9.64}$$

We first prove the property for the Landau (or Balescu-Lenard) equation. We use the explicit form (6.26) of the collision term and perform operations similar to those of Eq. (9.43) (symmetrization and partial integration):

$$\int d1\,\psi_n(1)\,\mathcal{K}\{f\,f\}$$

$$= \frac{8\pi^4}{m^2}\int d1\,d2\int d\mathbf{k}\,\psi_n(1)\,\delta(\mathbf{q}_1 - \mathbf{q}_2)\,\tilde{V}^2(k)\,\mathbf{k}\cdot\partial_{12}\delta(\mathbf{k}\cdot\mathbf{g})\,\mathbf{k}\cdot\partial_{12}\,f(1)f(2)$$

$$= \frac{4\pi^4}{m^2}\int d1\,d2\int d\mathbf{k}\,[\psi_n(1) + \psi_n(2)]\,\delta(\mathbf{q}_1 - \mathbf{q}_2)\,\tilde{V}^2(k)\,\mathbf{k}\cdot\partial_{12}\delta(\mathbf{k}\cdot\mathbf{g})\,\mathbf{k}\cdot\partial_{12}\,f(1)f(2)$$

$$= -\frac{4\pi^4}{m^2}\int d1\,d2\int d\mathbf{k}\,\tilde{V}^2(k)\,\{\delta(\mathbf{q}_1 - \mathbf{q}_2)\,\delta(\mathbf{k}\cdot\mathbf{g})\,\mathbf{k}\cdot\partial_{12}\,[\psi_n(1) + \psi_n(2)]\}$$

$$\times \mathbf{k} \cdot \partial_{12} f(1) f(2) \tag{9.65}$$

This expression is zero, *whatever the form of the RDF* whenever the expression enclosed in curly brackets vanishes:

$$\delta(\mathbf{q}_1 - \mathbf{q}_2) \, \delta(\mathbf{k} \cdot \mathbf{v}_1 - \mathbf{k} \cdot \mathbf{v}_2) \, [\mathbf{k} \cdot \partial_1 \psi_n(1) - \mathbf{k} \cdot \partial_2 \psi_n(2)] = 0 \,. \tag{9.66}$$

This equation has the following solutions [denoting by $\psi(\mathbf{q})$ an arbitrary function of $\mathbf{q}$]:

a) $\psi_1(\mathbf{q}, \mathbf{v}) = \psi(\mathbf{q})$, i.e., a function independent of $\mathbf{v}$. Then each term in the square brackets is zero.

b) $\psi_{2,3,4}(\mathbf{q}, \mathbf{v}) = [v_x, v_y, v_z] \, \psi(\mathbf{q})$, i.e. any component of the velocity, multiplied by $\psi(\mathbf{q})$. The square bracketted expression then reduces to:

$$[k^s \psi(\mathbf{q}_1) - k^s \psi(\mathbf{q}_2)] \,, \quad s = x, y, z.$$

This expression is zero because of the delta function $\delta(\mathbf{q}_1 - \mathbf{q}_2)$.

c) $\psi_5(\mathbf{q}, \mathbf{v}) = v^2 \, \psi(\mathbf{q})$, i.e., a function proportional to the square of the absolute value of $\mathbf{v}$. The square bracketted expression is now:

$$2 \, [\mathbf{k} \cdot \mathbf{v}_1 \, \psi(\mathbf{q}_1) - \mathbf{k} \cdot \mathbf{v}_2 \, \psi(\mathbf{q}_2)]$$

This vanishes because of the two delta functions. It can be shown that these five functions are the only solutions of Eq. (9.66).

Finally, we note that the Boltzmann collision term admits the same five collisional invariants as the Landau collision term. Indeed, consider functions $\psi_n(\mathbf{v})$ of the velocity (that may be multiplied by an arbitrary function of the position). Their average rate of change due to the collisions is calculated in a way similar to (9.41), by performing the appropriate symmetrizations (for brevity, we do not write the argument $\mathbf{q}$ in f):

$$
\begin{aligned}
\partial_t^{(col)} \langle \psi \rangle &= 2\pi \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, \psi(\mathbf{v}_1) \, \{f(\mathbf{v}_1'; t) f(\mathbf{v}_2'; t) - f(\mathbf{v}_1; t) f(\mathbf{v}_2; t)\} \\
&= \frac{\pi}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 \, db \, bg \, [\psi(\mathbf{v}_1) + \psi(\mathbf{v}_2) - \psi(\mathbf{v}_1') - \psi(\mathbf{v}_2')] \\
&\quad \times \{f(\mathbf{v}_1'; t) f(\mathbf{v}_2'; t) - f(\mathbf{v}_1; t) f(\mathbf{v}_2; t)\}
\end{aligned} \tag{9.67}
$$

This equation vanishes identically whenever the expression enclosed in square brackets vanishes. This happens for $\psi_n = 1, v_x, v_y, v_z, v^2$: except for the trivial case of a constant, this follows from Eqs. (7.35) expressing the conservation of momentum and energy in the collision process.

We thus found that, up to an arbitrary function of the position $\psi(\mathbf{q})$, *there exist exactly five collisional invariants for the kinetic equations.* Clearly, these five invariants express the *conservation of the number of particles, of the three components of the momentum and of the kinetic energy during a collision.* [8] More precisely speaking, the collisional invariance in an inhomogeneous system implies that the momentum and the energy lost by one of the collision partners is transferred to the other partner *at the same point* $\mathbf{q}$. This is a consequence of the localization arising from the ordering introduced by Assumption D) of Sec. 9.1.

9.7   Bibliographical Notes BN9

~~The modern developments of statistical dynamics, in particular, the derivation of~~ kinetic equations from microscopic dynamics, started in the mid-century with the following works:

Bogolioubov, N.N., 1946 (BN5),
van Hove, L., 1955, Physica, **21**, 517; 1957, Physica, **23**, 441,
Brout, R. and Prigogine, I., 1956, Physica, **22**, 621,
Prigogine, I. and Balescu, R., 1959, Physica, **25**, 281, 302; 1960, Physica, **23**, 145,
Prigogine, I. and Résibois, P., 1961, Physica, **27**, 629,
Résibois, P., 1961, Physica, **27**, 541.

The theory of *random walks* and *Brownian motion* was at the origin of the modern theory of stochastic processes. It was initiated by:

Einstein, A., 1905, Ann. d. Physik, **17**, 549;   1906, *ibid.*, **19**, 371,
v. Smoluchowski, M., 1906, Ann. d. Physik, **21**, 756.

A collection of these historical works appears in:

Fürth, R. (editor), 1956, *Investigations on the Theory of Brownian Motion*, Dover, New York.

The *Fokker-Planck equation* was first derived in:

Fokker, A.D., 1914, Ann. d. Physik, **43**, 812,
Planck, M., 1917, Sitz.Ber. d. Preuss. Akademie, p. 324.

The modern theory of *stochastic processes* is covered in many books and review papers. Among the references that are easily accessible to the average physicist, we may quote:

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[8]The number of collisional invariants depends on the type of system considered. For a multi-component system, this number exceeds 5, because there are additional conserved quantities. For instance, for the electron-ion plasma considered in Sec. 5.3 and in Chap. 8, there are six collisional invariants, corresponding to the number of electrons, the number of ions (which are separately conserved), the total momentum of the electrons and the ions, and their total energy.

Chandrasekhar, S., 1943, Rev. Mod. Phys., **15**, 851; reprinted (together with other papers on Brownian motion and applications to astrophysics) in: S. Chandrasekhar, 1989, *Selected Papers*, vol. **3**, p. 180, Univ. Chicago Press, Chicago,

Onsager, L. and Machlup, 1953, Phys. Rev., **91**, 1505, 1512,

Kubo, R., 1963, J. Math. Phys., **4**, 174,

Feller, W., 1971, *An Introduction to Probability Theory and its Applications*, vol. **2**, Wiley, New York,

Résibois, P. and De Leener, 1977 (**BN7**),

van Kampen, N.G., 1981, *Stochastic Processes in Physics and Chemistry*, North Holland, Amsterdam,

Gardiner, C.W.,1985, *Handbook of Stochastic Methods*, (2-nd edition; 4-th printing: 1997), Springer, Berlin,

Risken, H., 1989, *The Fokker-Planck Equation*, Springer, Berlin.

The H-theorem was first derived by Boltzmann, 1872 (**BN7**).

The classical objections ("Einwände") presented to Boltzmann were formulated by:

Loschmidt, J., 1876, Wien. Berichte, **73**, 139; 1877, ibid. **75**, 67,

Zermelo, 1896, Ann. Physik, **57**, 485.

An old, but still very inspiring discussion of Boltzmann's ideas is:

Ehrenfest, P. and T., 1911, in: *Enzyklopaedie der math. Wissenschaften*, vol. IV, Pt. 32, Leipzig; [english transl.: *The Conceptual Foundation of the Statistical Approach in Mechanics*, 1959, Cornell Univ. Pr., Ithaca].

The *collisional invariants* are discussed in all references about the Boltzmann equation (**BN7**); we add the following reference where the uniqueness of the collisional invariants is proved:

Grad, H., 1949, Comm. Pure Appl. Math., **2**, 311.

We mention here a few extensions of kinetic theory for systems other than the ones treated in Chaps.6 -9 (and the extensions of the Boltzmann equation discussed in **BN7**).

A very elegant treatment has been devised for a molecular theory of *Brownian motion* of a heavy test particle in a fluid (see Chaps. 11, 12). There exists again a small parameter: the ratio m/M of the masses of a fluid particle and the test particle. The Fokker-Planck equation can then be derived as an expansion in this parameter:

Lebowitz, J.L. and Rubin, E., 1963, Phys. Rev., **131**, 2381,

Résibois, P. and Davis, T., 1964, Physica, **30**, 1077,

Résibois, P. and Lebowitz, J.L., 1965, Phys. Rev., **139**, A1101.

The kinetic equations for phonon-phonon interactions in *solids* was derived by:

Peierls, R., 1929, Ann. Physik, **3**, 1055,

Peierls, R., 1955, *Quantum Theory of Solids*, Clarendon Pr., Oxford,

Prigogine, I. and Henin, F., 1960, J. Math. Phys., **1**, 349.

Kinetic equations for *liquids* have been derived by:

Rice, S.A. and Allnatt, A.R., 1961, J. Chem. Phys., **34**, 2144, 2156,

Prigogine, I., Nicolis, G. and Misguich, J.H., 1965, J. Chem. Phys., **43**, 4516,

Allen, P.M. and Cole, G.H.A., 1968, Mol. Phys., **15**, 549, 557,

Misguich, J.H. and Nicolis, G., 1972, Mol. Phys., **24**, 309.

Magnetic systems, modelled as a collection of *Heisenberg spins* on a lattice were studied in non-equilibrium situations by:

~~Résibois, P. and De Leener, M.~~, 1966, Phys. Rev., **152**, 305, 318;   1969, *ibid.*, **178**, 806.

Chapter 10

Hydrodynamics and Transport

10.1 The Hydrodynamic Quantities

The most important practical purpose of statistical dynamics is the implementation of the following program:

- *The derivation of the macroscopic equations of continuum mechanics, (e.g., of hydrodynamics, electrodynamics,...) from the microscopic laws of evolution, i.e. from the kinetic equations;*

- *The assessment of the limits of validity of the former, and their possible generalization;*

- *The determination of the phenomenological constants of the hydrodynamical equations, i.e., the* TRANSPORT COEFFICIENTS, *from the microscopic properties of the molecules and their interaction law.*

In other words, statistical dynamics provides us with the link between the microscopic, molecular level of description (distribution functions, kinetic equations) and the macroscopic, continuum level (hydrodynamic quantities and evolution laws). The latter were briefly reviewed in Sec. 2.2.

We begin with the definition of the *hydrodynamic quantities,* which are local quantities, i.e., *fields,* defined in each point x of the three-dimensional physical space, and at each time t. By definition, the hydrodynamical quantities are the densities of the conserved quantities, i.e.: *mass, momentum* and *energy.*

We know that every local quantity (density) is defined in statistical mechanics as the average of a dynamical function having the following characteristic form:

$$B(\mathbf{x},t) = \int d\mathbf{v} \int d\mathbf{q} \ \beta(\mathbf{v}) \, \delta(\mathbf{x} - \mathbf{q}) \, f(\mathbf{q}, \mathbf{v}; t),$$

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which can also be written as follows:

$$B(\mathbf{x},t) = \int d\mathbf{v}\, \beta(\mathbf{v})\, f(\mathbf{v};\mathbf{x},t)\,. \tag{10.1}$$

We introduced here the concept of a *local RDF*:

$$f(\mathbf{v};\mathbf{x},t) = \int d\mathbf{q}\, \delta(\mathbf{x}-\mathbf{q})\, f(\mathbf{q},\mathbf{v};t)\,. \tag{10.2}$$

The difference between $f(\mathbf{v};\mathbf{x},t)$ and $f(\mathbf{q},\mathbf{v};t)$ may seem trivial; nevertheless, the ~~change of outlook simplifies the forthcoming~~ calculations: the averaging operation involves only the velocity space. The local distribution function can also be envisaged from a different point of view: with each point $(\mathbf{x},t)$ of the physical space-time it associates a function of $\mathbf{v}$. It could therefore be called "a field of distribution functions".

The hydrodynamical quantities are defined by an appropriate choice of the dynamical functions $\beta(\mathbf{v})$. The following definitions are evident.

Mass density $\rho(\mathbf{x},t)$:

$$\rho(\mathbf{x},t) = m \int d\mathbf{v}\, f(\mathbf{v};\mathbf{x},t)\,, \tag{10.3}$$

Momentum density $\rho(\mathbf{x},t)\,\mathbf{u}(\mathbf{x},t)$ and local velocity $\mathbf{u}(\mathbf{x},t)$:

$$\rho(\mathbf{x},t)\,\mathbf{u}(\mathbf{x},t) = m \int d\mathbf{v}\, \mathbf{v}\, f(\mathbf{v};\mathbf{x},t)\,, \tag{10.4}$$

Internal energy density $\rho(\mathbf{x},t)\,e(\mathbf{x},t)$:

$$\rho(\mathbf{x},t)\,e(\mathbf{x},t) = \tfrac{1}{2}m \int d\mathbf{v}\, |\mathbf{v}-\mathbf{u}|^2\, f(\mathbf{v};\mathbf{x},t)\,. \tag{10.5}$$

Note that the thermodynamic internal energy is defined as the total energy (average of $mv^2/2$) minus the average macroscopic kinetic energy $mu^2/2$; it is therefore not a conserved quantity. The average velocity $\mathbf{u}$ is the quantity defined by (10.4): it depends on $\mathbf{x},t$, but we omit writing these arguments, for brevity.

We define three additional hydrodynamic quantities:

Number density (number of particles per unit volume) $n(\mathbf{x},t)$:

$$n(\mathbf{x},t) = \int d\mathbf{v}\, f(\mathbf{v};\mathbf{x},t)\,,. \tag{10.6}$$

Particle flux $\Gamma(\mathbf{x},t)$:

$$\Gamma(\mathbf{x},t) \equiv n(\mathbf{x},t)\,\mathbf{u}(\mathbf{x},t) = \int d\mathbf{v}\, \mathbf{v}\, f(\mathbf{v};\mathbf{x},t)\,, \tag{10.7}$$

Pressure $P(\mathbf{x},t)$ and Temperature $T(\mathbf{x},t)$:

$$P(\mathbf{x}, t) = n(\mathbf{x}, t)\, T(\mathbf{x}, t) = \tfrac{1}{3}m \int d\mathbf{v}\, |\mathbf{v} - \mathbf{u}|^2\, f(\mathbf{v}; \mathbf{x}, t)\,. \tag{10.8}$$

Note that the *kinetic temperature* introduced here is an extension of the thermodynamic temperature: the latter is only defined in equilibrium.

Eq. (10.8) is actually just the *equation of state* for the pressure of a perfect gas [see Eq. (2.5)]. Similarly, combining (10.5) and (10.8), we find:

$$\rho(\mathbf{x}, t)\, e(\mathbf{x}, t) = \tfrac{3}{2} n(\mathbf{x}, t)\, T(\mathbf{x}, t), \tag{10.9}$$

which is the equation of state for the internal energy of a perfect gas [Eq. (2.5)]. Eqs. (10.8), (10.9) are approximations valid for the three kinetic equations discussed in previous chapters, but which should be revised in more general cases.

It is worth stressing that *the two equations of state do not involve the velocity* **u** (this was also mentioned in Sec. 2.2). This is due to the subtraction of **u** in the definitions (10.5) and (10.8), which take out the convective part of the energy, i.e., $\tfrac{1}{2}\rho u^2$.

From here on we shall always *measure the temperature T in energy units* (Joules, calories, electron-volts,...). Thus, if $\widetilde{T}$ is the temperature measured in Kelvin degrees, $T = k_B \widetilde{T}$, where k_B is Boltzmann's constant measured in the appropriate energy units. This convention leads to simpler and clearer formulae.

We also write here the formulae for two *non-hydrodynamical quantities* that play a very important role in hydrodynamics; their definition follows from the derivation of the balance equations performed in the next section:

Dissipative pressure tensor $\pi(\mathbf{x}, t)$:

$$\pi_{rs}(\mathbf{x}, t) = m \int d\mathbf{v}\, (v_r - u_r)(v_s - u_s)\, f(\mathbf{v}; \mathbf{x}, t) - \delta_{rs} P(\mathbf{x}, t)\,. \tag{10.10}$$

[The total pressure tensor, $\pi_{rs}(\mathbf{x}, t) + \delta_{rs} P(\mathbf{x}, t)$ is also identified with the *momentum flux*: the integrand has the form of a relative momentum $m(v_s - u_s)$ carried with a velocity $(v_r - u_r)$].

Heat flux[1]: $\mathbf{q}(\mathbf{x}, t)$:

$$q_r(\mathbf{x}, t) = \tfrac{1}{2}m \int d\mathbf{v}\, (v_r - u_r)\, |\mathbf{v} - \mathbf{u}|^2\, f(\mathbf{v}; \mathbf{x}, t)\,. \tag{10.11}$$

[This has the form of relative kinetic energy $\tfrac{1}{2}m |\mathbf{v} - \mathbf{u}|^2$ carried with velocity $(v_r - u_r)$].

We finally rewrite the *kinetic equation* in the slightly different form appropriate for the local distribution function [$\nabla = \partial/\partial \mathbf{x}$]:

---

[1] No confusion should arise between the phase space co-ordinate $\mathbf{q}$ and the field denoting the heat flux, $\mathbf{q}(\mathbf{x}, t)$.

$$\partial_t f(\mathbf{v}; \mathbf{x}, t) = -\mathbf{v} \cdot \nabla f(\mathbf{v}; \mathbf{x}, t) + \mathcal{K} \{f f\} \,. \tag{10.12}$$

We also recall the existence of the five collisional invariants:

$$\int d\mathbf{v}\, \mathcal{K} = 0\,,$$

$$\int d\mathbf{v}\, v_r\, \mathcal{K} = 0\,, \quad r = x, y, z\,,$$

$$\int d\mathbf{v}\, v^2\, \mathcal{K} = 0\,. \tag{10.13}$$

In conclusion, we arrive at the following description of the dynamical systems in the framework of kinetic theory. The *state* of the system is defined by the local distribution function $f(\mathbf{v}; \mathbf{x}, t)$; the *dynamical functions* are functions of the velocity: $\beta(\mathbf{v})$; the *law of evolution* is the kinetic equation (10.12).

10.2   The Hydrodynamical Balance Equations

In Chap. 2 we recalled the hydrodynamical balance equations (2.2) - (2.4) that are derived in macroscopic physics as consequences of the conservation of matter, momentum and energy. We now show that these equations are easily derived from the basic kinetic equation (10.12). The idea is simple: the hydrodynamic quantities ρ, $\mathbf{u}$, e are defined by Eqs. (10.3) - (10.5) as *moments of the local RDF*, i.e., averages of dynamical functions that are polynomials in the components of $\mathbf{v}$. In order to obtain equations of evolution for the moments, it suffices to multiply both sides of Eq. (10.12) by the appropriate polynomial, and to integrate over the velocity. We illustrate the procedure by two examples.

In order to obtain the continuity equation (2.2), we consider the trivial moment m, i.e., a constant. Noting that a constant is a collisional invariant, it follows from (10.13) that the collision term gives a vanishing contribution, hence:

$$\partial_t \int d\mathbf{v}\, m\, f(\mathbf{v}; \mathbf{x}, t) = -\int d\mathbf{v}\, m\, \mathbf{v} \cdot \nabla f(\mathbf{v}; \mathbf{x}, t) + 0\,.$$

Using the definitions (10.3) and (10.4), we note that the left hand side is simply $\partial_t \rho$ and that the right hand side can be transformed as follows:

$$-\int d\mathbf{v}\, m\, \mathbf{v} \cdot \nabla f(\mathbf{v}; \mathbf{x}, t) = -\nabla \cdot \int d\mathbf{v}\, m\, \mathbf{v}\, f(\mathbf{v}; \mathbf{x}, t) = -\nabla \cdot (\rho \mathbf{u})\,;$$

this proves Eq. (2.2).

To obtain the momentum balance equation, we consider the moment $m v_r$. This is also a collisional invariant, hence only the free flow contributes to its evolution:

$$\partial_t \rho u_r = -\int d\mathbf{v}\, m\, v_r\, v_s \nabla_s\, f(\mathbf{v}; \mathbf{x}, t) = -\nabla_s \int d\mathbf{v}\, m\, v_r v_s\, f(\mathbf{v}; \mathbf{x}, t)$$

$$= -\nabla_s \int d\mathbf{v}\, [m\, u_r u_s + m\, (v_r - u_r)(v_s - u_s)]\, f(\mathbf{v}; \mathbf{x}, t)$$

$$= -\nabla_s\, [\rho\, u_r u_s + P\, \delta_{rs} + \pi_{rs}]$$

In the third step we added and subtracted $m\, u_r u_s$ to the integrand in order to exhibit the convective term. In the last step we used the definition (10.10), thus confirming the identification of that quantity with the pressure tensor. The internal energy balance is derived in a similar way.

We have thus shown that *the kinetic equation* (10.12) *leads quite directly to the hydrodynamical balance equations*, which we rewrite here, for convenience:

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}) , \qquad (10.14)$$

$$\partial_t \rho \mathbf{u} = -\nabla \cdot [\rho \mathbf{u}\mathbf{u} + P \mathsf{I} + \pi] , \qquad (10.15)$$

$$\partial_t \rho e = -\nabla \cdot [\rho e \mathbf{u} + \mathbf{q}] - P \nabla \cdot \mathbf{u} - \pi : \nabla \mathbf{u} . \qquad (10.16)$$

We know from Sec. 2.2 that the hydrodynamical balance equations are not a closed set. Thus, the equation for ρ requires the knowledge of $\mathbf{u}$, the equation for $\mathbf{u}$ requires the knowledge of the *non-hydrodynamical quantity* π, and so on. From the microscopic point of view, this open character becomes clearer. Let us call a *moment of order* n the average value of a monomial of order n in the components of the velocity. We then discover the following structure:

The equation of evolution of any moment of order n necessarily involves a moment of order $n + 1$ (as well as possibly higher order moments).

We see again here this general characteristic property of the basic equations of statistical physics: a *hierarchical structure*. It is, however, important to note the following point. The hierarchical structure of the BBGKY equations is due to the presence of the interactions. The structure of the hydrodynamical balance equations is due to the form of the *free flow term*, *which introduces an additional factor* $\mathbf{v}$ into all averages. The interactions will, however, also play a role: the higher moments that are added to the hierarchy are no longer collisional invariants: the collision term introduces additional higher order moments into the equations of evolution.We thus formulate the BASIC PROBLEM OF HYDRODYNAMICS:

How, and under what conditions can the non-hydrodynamical quantities (such as π, $\mathbf{q}$) *be expressed as functionals of the hydrodynamical moments* ρ, $\mathbf{u}$, T ?

At the macroscopic level this problem is solved by using symmetry arguments and phenomenological relations taken from experimental evidence: this leads to transport

equations such as (2.6) which introduce undetermined constant *transport coefficients.* It is here that statistical dynamics exhibits its richness: kinetic theory offers the means for treating this problem in a fundamental way, more completely and more systematically than macroscopic physics. It provides us with explicit expressions of the transport coefficients in terms of the properties of the underlying molecules. It also determines the limits of validity of the transport equations (2.6), as well as their possible generalizations. All these problems form the domain of a huge and important discipline: TRANSPORT THEORY. The latter can be considered as the final accomplishment of the programme of statistical dynamics. Its classical methodology will be illustrated here only for a few very simple cases. Additional aspects of transport theory are treated in the forthcoming chapters.

10.3   Diffusion and Heat Conduction

We now define more precisely the simple problem we want to study. In a one-component fluid, the closure of the hydrodynamical equations requires the determination of three transport coefficients appearing in Eqs. (2.6): the heat conductivity κ and the two viscosity coefficients η and ζ. The former can be determined independently of the latter two, because it relates to a vectorial flux, whereas the pressure tensor (i.e. the momentum flux) is a tensorial quantity which cannot be coupled to the heat flux in a linear theory. For brevity and simplicity we do not discuss here the problem of the viscosity.

The remaining, one-component inviscid fluid model is sufficient for the calculation of the heat conductivity. We should like, however, to illustrate the coupling of several fluxes (in particular: several vectorial fluxes) in order to make contact with the non-trivial laws of nonequilibrium thermodynamics. This situation prevails in a many-component fluid, such as a mixture of gases or an electron-ion plasma. A new irreversible phenomenon appears here: DIFFUSION, produced by an inequality of density, or pressure or chemical potential between the two species. This is a very important process in practice; it is also very much studied in statistical dynamics, being the simplest transport coefficient. We will frequently meet with this problem in forthcoming pages.

We consider an even simpler problem by introducing diffusion in a one-component system: this process is sometimes called *self-diffusion.* Within such a system we consider a population of *tagged particles* (also called *test particles*) that are mechanically identical with those of the *bath*, but that can be distinguished from the latter by having a slightly different phase space distribution. We may assume that the bath particles are in a state of local equilibrium. Moreover, the number of tagged particles is assumed very small compared to the number of bath particles. As a result the collisions between tagged particles can be neglected: they only collide with bath

particles. On the other hand, the equilibrium of the bath particles will hardly be disturbed by the few collisions with the tagged ones. The problem to be solved is thus the evolution to equilibrium of the tagged particle population, described by a local RDF: $f(\mathbf{v}; \mathbf{x}, t)$. The kinetic equation for these particles is thus:

$$\partial_t f + \mathbf{v} \cdot \nabla f = \mathcal{K}\{f, f_b\} \tag{10.17}$$

Here f_b is the RDF of the bath particles, assumed to be a local Maxwellian (9.63), for which we assume space and time dependent density and temperature, but vanishing average velocity:

$$f_b(\mathbf{v}; \mathbf{x}, t) = n_b(\mathbf{x}, t) \left[\frac{m}{2\pi T(\mathbf{x}, t)}\right]^{3/2} \exp\left[-\frac{mv^2}{2T(\mathbf{x}, t)}\right]. \tag{10.18}$$

The test particle distribution is a non-equilibrium distribution of the form:

$$f(\mathbf{v}; \mathbf{x}, t) = n(\mathbf{x}, t) \left[\frac{m}{2\pi T(\mathbf{x}, t)}\right]^{3/2} \exp\left[-\frac{mv^2}{2T(\mathbf{x}, t)}\right] \{1 + \overline{\chi}(\mathbf{v}; \mathbf{x}, t)\}. \tag{10.19}$$

An important simplification has appeared here as a consequence of our assumptions: the collision term $\mathcal{K}\{f, f_b\}$ is *linearized*: as it describes collisions of the test particles only with the bath particles (and not with other test particles), the unknown f enters linearly the collision integral. We also note that the latter is no longer symmetric in the two "species" of particles.

The macroscopic balance equations for the number density (10.6) and the internal energy density[2] (10.5) for the test particles are:

$$\partial_t n = -\nabla \cdot \mathbf{\Gamma}, \tag{10.20}$$

where $\mathbf{\Gamma}$ is the particle flux defined in Eq. (10.7), and:

$$\partial_t ne = -\nabla \cdot (ne\mathbf{u} + P\mathbf{u} + \mathbf{q}) - \mathbf{u} \cdot \nabla P + \overline{Q}^{(2)}. \tag{10.21}$$

For convenience, we have slightly rearranged the terms in Eq. (10.16) by including the term $P\mathbf{u}$ into the energy flux; the source term $-\mathbf{u} \cdot \nabla P$ now clearly represents the rate of work done by the pressure force $-\nabla P$. As stated above, the dissipative pressure tensor π is neglected. Eq. (10.21) can be transformed into an equation for the temperature by using the two equations of state for an ideal gas: $P = nT$ and $ne = \frac{3}{2}nT$:

$$\partial_t \tfrac{3}{2} nT = -\nabla \cdot \left(\tfrac{5}{2} T \mathbf{\Gamma} + \mathbf{q}\right) - \mathbf{u} \cdot \nabla P + \overline{Q}^{(2)}. \tag{10.22}$$

---

[2] Note that e is defined here as internal energy per particle.

As compared to Eq. (10.16) we see here a new term $\overline{Q}^{(2)}$ representing the collisional rate of change of the internal energy. This term arises because in the present problem neither the energy nor the momentum of the test particles are collisional invariants: these quantities can be exchanged with the bath molecules: only the *total* energy and momentum (test particles plus bath particles) are invariant. Thus, the only collisional invariant of the test particle system is its number density. This statement can be checked explicitly: in Eq. (9.65) the RDF's $f(1), f(2)$ are no longer the same, hence the symmetrization can no longer be performed.

Our main purpose will be the determination of the non-hydrodynamical vector fluxes Γ (particle flux) and q [heat flux, Eq. (10.11)][3]. Several methods were developed since the beginning of this century for the solution of the kinetic equations and the determination of the transport coefficients. We use here a very simple, transparent and efficient procedure, first introduced (in a rather different form) by H. Grad: the HERMITIAN MOMENT METHOD. A rather exhaustive description of the method can be found in the author's book on Transport Processes in Plasmas (RB-3); here we only give a short account for illustration.

The idea of the method is quite similar to the perturbation theory of quantum mechanics. We recall that all our derivations for inhomogeneous systems are done under the assumption of smallness of the parameter λ_H defined in Eq. (6.8). This defines a HYDRODYNAMIC REGIME, in which the collisional mean free path is very short compared to the hydrodynamical length (see Sec. 6.2). The latter is related to the length of the gradients of the hydrodynamical quantities:

$$l_T^{-1} = \frac{|\nabla T|}{T}, \quad l_n^{-1} = \frac{|\nabla n|}{n}; \quad l_H = \min(l_T, l_n). \tag{10.23}$$

Associated with these length scales are the corresponding time scales:

$$\tau_T^{-1} = \left(\frac{T}{m}\right)^{1/2} \frac{|\nabla T|}{T}, \quad \tau_n^{-1} = \left(\frac{T}{m}\right)^{1/2} \frac{|\nabla n|}{n}; \quad \tau_H = \min(\tau_T, \tau_n). \tag{10.24}$$

In order to close Eqs. (10.20), (10.21), we write the equations of evolution for the particle flux vector Γ_r and for the heat flux vector q_r. The former is immediately obtained from (10.15), by changing the mass density ρ to the particle density n, and adding a collisional rate of change of the momentum of the tagged particles (because the latter is not a collisional invariant!). The equation of evolution of the heat flux is obtained from (10.11) by the same procedure as the other balance equations of Sec. 10.2. Neglecting all terms that are small in the hydrodynamical regime (i.e., terms

---

[3]The collisional energy exchange rate $\overline{Q}^{(2)}$ can also be obtained by the methods developed below: we shall, however, not discuss it explicitly here.

of relative order λ_H^2) we obtain the following equations[4]:

$$\partial_t \Gamma_r = -m^{-1} \nabla_r P + \overline{Q}_r^{(1)}, \tag{10.25}$$

$$\partial_t q_r = -\frac{5}{2} n \frac{T}{m} \nabla_r T + \overline{Q}_r^{(3)}. \tag{10.26}$$

These equations have a clear meaning. The change in time of the vector fluxes is due to a competition between the gradients of the hydrodynamical quantities P and T and the effect of the collisions $\overline{Q}_r^{(p)}$, $(p = 1, 3)$; the latter quantities are called *generalized friction forces* (these quantities will be formally defined below). Note that the two terms in the right hand sides act on different time scales. The first terms, related to the gradients, are proportional to τ_H^{-1}, whereas the collisional terms act on the relaxation time scale, τ_R^{-1}. In the final stationary state these two contributions must equilibrate each other and produce steady fluxes of particles and heat. In order that such an equilibration be possible it is necessary that the generalized frictions $\overline{Q}_r^{(p)}$ be of order $(\tau_R/\tau_H) = \lambda_H$, i.e., they are first order quantities in the small *hydrodynamic parameter* λ_H.

10.4   The Hermitian Moment Expansion

We now go back to Eqs. (10.18), (10.19) and introduce the new dimensionless variable c:

$$c_r = \left[\frac{m}{T(\mathbf{x}, t)}\right]^{1/2} v_r. \tag{10.27}$$

We also define the reference distribution function $\phi^0(c)$ as follows:

$$\phi^0(c) = (2\pi)^{-3/2} \exp(-\tfrac{1}{2} c^2), \tag{10.28}$$

which is normalized to one:

$$\int d\mathbf{c}\, \phi^0(c) = 1. \tag{10.29}$$

The distribution functions (10.18), (10.19) are now written in the form:

$$f_b(\mathbf{v}; \mathbf{x}, t) = n_b(\mathbf{x}, t) \left[\frac{m}{2\pi T(\mathbf{x}, t)}\right]^{3/2} \phi^0(c), \tag{10.30}$$

---

[4]In deriving Eq. (10.26), use is made of the ideal monoatomic gas value of the specific heat per particle at constant volume: $c_V = \frac{3}{2} k_B$.

$$f(\mathbf{v}; \mathbf{x}, t) = n(\mathbf{x}, t) \left[\frac{m}{2\pi T(\mathbf{x}, t)} \right]^{3/2} \phi^0(c) \left\{ 1 + \chi(\mathbf{c}; \mathbf{x}, t) \right\} . \qquad (10.31)$$

The deviation from equilibrium $\chi(\mathbf{c}; \mathbf{x}, t)$ (which is the actual unknown in our problem) is assumed to be small, i.e., $|\chi(\mathbf{c}; \mathbf{x}, t)| = O(\lambda_H)$. In order to make Eq. (10.31) well defined, we must say something about the functions $n(\mathbf{x}, t)$, $T(\mathbf{x}, t)$. In the state of local equilibrium, these functions coincide precisely with the particle density and the temperature as defined by Eqs. (10.6), (10.8). This will no longer be true in an arbitrary nonequilibrium state, unless we *require* it by introducing the following conditions:

$$
\begin{aligned}
\int d\mathbf{v} \, f(\mathbf{v}; \mathbf{x}, t) &= \int d\mathbf{v} \, f^0(\mathbf{v}; \mathbf{x}, t) = n(\mathbf{x}, t) , \\
\tfrac{1}{3} m \int d\mathbf{v} \, |\mathbf{v} - \mathbf{u}|^2 \, f(\mathbf{v}; \mathbf{x}, t) &= \tfrac{1}{3} m \int d\mathbf{v} \, |\mathbf{v} - \mathbf{u}|^2 \, f^0(\mathbf{v}; \mathbf{x}, t) = n(\mathbf{x}, t) T(\mathbf{x}, t) .
\end{aligned}
$$
$$(10.32)$$

We are allowed to introduce these conditions, because n and T are arbitrary constants in the local equilibrium RDF (see Sec. 9.5). Eqs. (10.32) express the following *constraints* on the deviation χ:

$$\int d\mathbf{c} \, \phi^0 \chi = 0 , \quad \int d\mathbf{c} \, c^2 \phi^0 \chi = 0 . \qquad (10.33)$$

Proceeding now as in quantum mechanics, we expand the function χ on a complete orthogonal basis. Given the Gaussian form (10.28) of the reference RDF, the natural basis functions are the HERMITE POLYNOMIALS. As we are considering functions of three variables, c_x, c_y, c_z we need to use the so-called *irreducible tensorial Hermite polynomials*. These polynomials are classified according to their tensorial variance. We thus have scalar polynomials: $H^{(2n)}(\mathbf{c}) = P^{(n)}(c^2)$, vectorial polynomials of the form $H_r^{(2n+1)}(\mathbf{c}) = c_r R^{(n)}(c^2)$, traceless second rank tensors: $H_{rs}^{(2n+2)}(\mathbf{c}) = (c_r c_s - \tfrac{1}{3} c^2 \delta_{rs}) S^{(n)}(c^2)$, etc., where $P^{(n)}, R^{(n)}, S^{(n)}$, are polynomials of degree n in the (scalar) variable c^2. The expansion of $\chi(\mathbf{c}; \mathbf{x}, t)$ has the following general form:

$$
\begin{aligned}
\chi(\mathbf{c}; \mathbf{x}, t) = \sum_{n=0}^{\infty} \Big\{ & h^{(2n)}(\mathbf{x}, t) \, H^{(2n)}(\mathbf{c}) + h_r^{(2n+1)}(\mathbf{x}, t) \, H_r^{(2n+1)}(\mathbf{c}) \\
& + h_{rs}^{(2n+2)}(\mathbf{x}, t) \, H_{rs}^{(2n+2)}(\mathbf{c}) + ... \Big\} .
\end{aligned}
$$
$$(10.34)$$

The coefficients $h_{rs...}^{(p)}(\mathbf{x}, t)$ are called TENSORIAL HERMITIAN MOMENTS. According to the philosophy of perturbation theory, the study of the function $\chi(\mathbf{c}; \mathbf{x}, t)$ is approximated by the determination of a finite set of Hermitian moments. In practice,

the series (10.34) is truncated at some level. In our case, we wish to determine the *vectorial* quantities Γ_r, q_r; a simple symmetry argument shows that only vectorial moments can contribute to these quantities in a linear theory. We thus retain only the latter moments and truncate the series after the second Hermitian moment:

$$\chi(\mathbf{c}; \mathbf{x}, t) = h_r^{(1)}(\mathbf{x}, t)\, H_r^{(1)}(\mathbf{c}) + h_r^{(3)}(\mathbf{x}, t)\, H_r^{(3)}(\mathbf{c})\,. \tag{10.35}$$

This approximation will be sufficient for illustration purposes. Clearly, if good accuracy is required, one has to retain more moments in the series. It appears, however, that the series converges very fast after the fifth moment.

The vectorial Hermite polynomials have the following orthogonality property:

$$\int d\mathbf{c}\, \phi^{(0)}(\mathbf{c})\, H_r^{(2n+1)}(\mathbf{c})\, H_s^{(2m+1)}(\mathbf{c}) = \delta_{nm}\,\delta_{rs}\,. \tag{10.36}$$

The first two vectorial polynomials are:

$$H_r^{(1)}(\mathbf{c}) = c_r\,, \quad H_r^{(3)}(\mathbf{c}) = \frac{1}{\sqrt{10}}\, c_r\,(c^2 - 5)\,. \tag{10.37}$$

It follows from these relations that the Hermitian moment $h_r^{(1)}(\mathbf{x}, t)$ is very simply related to the test particle flux:

$$\Gamma_r = n \left(\frac{T}{m}\right)^{1/2} h_r^{(1)}(\mathbf{x}, t)\,, \tag{10.38}$$

For the heat flux, the relation is more subtle. It is easily checked (using the kinetic equation) that the quantity:

$$\Phi_r = \left(\frac{T}{m}\right)^{3/2} n \frac{m}{2} \int d\mathbf{c}\, c_r\, c^2\, \phi^{(0)} \chi \tag{10.39}$$

represents the *total energy flux*, i.e., the vector whose divergence appears in Eq.(10.22). In other words, it represents the sum of the convective energy flux $\frac{5}{2} T\, \Gamma$ and of the conductive heat flux $\mathbf{q}$. We rewrite this equation as follows:

$$\begin{aligned}
\Phi_r &= \sqrt{10} \left(\frac{T}{m}\right)^{3/2} n \frac{m}{2} \int d\mathbf{c}\, \left\{ \tfrac{1}{\sqrt{10}} c_r\, (c^2 - 5) + \tfrac{5}{\sqrt{10}}\, c_r \right\} \phi^{(0)} \chi \\
&= \sqrt{\tfrac{5}{2}} n m \left(\frac{T}{m}\right)^{3/2} h_r^{(3)} + \tfrac{5}{2} T\, \Gamma_r
\end{aligned} \tag{10.40}$$

Comparing this equation to (10.22) we see that the third order Hermitian moment is proportional to the true (conductive) heat flux:

$$q_r = \sqrt{\tfrac{5}{2}} n m \left(\frac{T}{m}\right)^{3/2} h_r^{(3)}\,. \tag{10.41}$$

The equations of evolution of the two Hermitian moments are easily derived from (10.25), (10.26):

$$\partial_t h_r^{(1)}(\mathbf{x}, t) = -\left(\frac{T}{m}\right)^{1/2} \frac{1}{nT} \nabla_r(nT) + Q_r^{(1)},$$

$$\partial_t h_r^{(3)}(\mathbf{x}, t) = -\sqrt{\tfrac{5}{2}} \left(\frac{T}{m}\right)^{1/2} \frac{1}{T} \nabla_r T + Q_r^{(3)} \tag{10.42}$$

The generalized frictions are defined as follows:

$$Q_r^{(2n+1)} = \frac{1}{n} \int d\mathbf{v} \, H_r^{(2n+1)} \left[\left(\frac{m}{T}\right)^{1/2} \mathbf{v} \right] \mathcal{K}\{f, f_b\} . \tag{10.43}$$

All the results obtained up to this point are completely general. From here on, the explicit form of the results, in particular of the generalized frictions, will depend on the collision term used in the calculation, hence on the type of system considered. We sketch below the calculations for the case of the *Landau kinetic equation for weakly coupled systems*. The calculations are significantly more complicated for the Boltzmann equation (see **BN10**).

The friction force $Q_r^{(1)}$ is evaluated using the form (6.31), (6.32) of the Landau collision term:

$$Q_r^{(1)} = \frac{n_b}{m^{1/2}T^{3/2}} \int d\mathbf{c}_1 d\mathbf{c}_2 \, c_{1r} \, \partial_{1m} G_{mn}(\gamma) \left(\partial_{1n} - \partial_{2n}\right)$$
$$\times \exp\left[-\tfrac{1}{2}\left(c_1^2 + c_2^2\right)\right]\left\{1 + h_s^{(1)}c_{1s} + h_s^{(3)}\tfrac{1}{\sqrt{10}}c_{1s}\left(c^2 - 5\right)\right\} . \tag{10.44}$$

where $\gamma = \mathbf{c}_1 - \mathbf{c}_2$, and $\partial_{1m} = \partial/\partial c_{1m}$. We also note the identity:

$$\gamma_m G_{mn}(\gamma) = G_{mn}(\gamma)\gamma_n = 0 . \tag{10.45}$$

Performing an integration by parts and expressing explicitly the derivatives $(\partial_{1n} - \partial_{2n})$ we obtain:

$$Q_r^{(1)} = -\frac{n_b}{m^{1/2}T^{3/2}} \int d\mathbf{c}_1 d\mathbf{c}_2 \, G_{rn}(\gamma) \exp\left[-\tfrac{1}{2}\left(c_1^2 + c_2^2\right)\right]$$
$$\times \left\{h_s^{(1)}\delta_{ns} + h_s^{(3)}\tfrac{1}{\sqrt{10}}\left[\left(c^2 - 5\right)\delta_{ns} + 2c_{1n}c_{1s}\right]\right\} . \tag{10.46}$$

The expression is easily evaluated by changing the integration variables to γ and $\Gamma = \tfrac{1}{2}\left(\mathbf{c}_1 + \mathbf{c}_2\right)$; we then note:

$$\mathbf{c}_1 = \Gamma + \tfrac{1}{2}\gamma, \quad \mathbf{c}_2 = \Gamma - \tfrac{1}{2}\gamma,$$
$$c_1^2 = \Gamma^2 + \gamma \cdot \Gamma + \tfrac{1}{4}\gamma^2, \qquad c_{1n}c_{1s} = \Gamma_n\Gamma_s + \tfrac{1}{2}\left(\gamma_n\Gamma_s + \gamma_s\Gamma_n\right) + \tfrac{1}{4}\gamma_n\gamma_s .$$

After substitution of these formulae into (10.46) and use of (10.45), the integrals are calculated by using the following equations for the Gaussian moments:

$$(2\pi)^{-3/2} \int d\Gamma\, e^{-\Gamma^2}\, \Gamma^{2k} = \frac{3.5...(2k+1)}{2^{k+3/2}} \,,$$

$$(2\pi)^{-3/2} \int d\Gamma\, e^{-\Gamma^2}\, \Gamma^{2k}\Gamma_m\Gamma_n = \frac{5.7...(2k+3)}{2^{k+5/2}}\, \delta_{mn} \,,$$

$$(2\pi)^{-3/2} \int d\Gamma\, e^{-\Gamma^2}\, \Gamma^{2k}\Gamma_m\Gamma_n\Gamma_p\Gamma_q = \frac{7.9...(2k+5)}{2^{k+7/2}}$$
$$\times \left(\delta_{mn}\delta_{pq} + \delta_{mp}\delta_{nq} + \delta_{mq}\delta_{np}\right) \,, \quad (10.47)$$

and for the integrals involving the Landau tensor:

$$(2\pi)^{-3/2} \int d\gamma\, e^{-\gamma^2/4}\, G_{rs}(\gamma)\, \gamma^{2k} = \frac{2^{2k+1}k!}{3\sqrt{2\pi}}\, B\, \delta_{rs}$$

$$(2\pi)^{-3/2} \int d\gamma\, e^{-\gamma^2/4}\, G_{rs}(\gamma)\, \gamma^{2k}\gamma_m\gamma_n = \frac{2^{2k+2}(k+1)!}{15\sqrt{2\pi}}\, B$$
$$\times \left(4\delta_{rs}\delta_{mn} - \delta_{rm}\delta_{sn} - \delta_{rn}\delta_{sm}\right) \quad (10.48)$$

[The factor B was defined in (6.30)]. Collecting all these results, a short calculation leads to the result:

$$Q_r^{(1)} = -\frac{1}{3\sqrt{\pi}}\frac{Bn_b}{m^{1/2}T^{3/2}} \left[h_r^{(1)} - \frac{3}{2\sqrt{10}}\, h_r^{(3)}\right] \,. \quad (10.49)$$

A similar, somewhat longer calculation yields:

$$Q_r^{(3)} = -\frac{1}{3\sqrt{\pi}}\frac{Bn_b}{m^{1/2}T^{3/2}} \left[-\frac{3}{2\sqrt{10}}h_r^{(1)} + \frac{75}{40}\, h_r^{(3)}\right] \,. \quad (10.50)$$

The generalized frictions thus appear as linear combinations of the Hermitian moments. The prefactor in these equations has the dimensions of an inverse time: it is clearly to be identified with the inverse relaxation time $\widehat{\tau}_R^{-1}$ (or the *collision frequency*); we thus introduce the provisional notation:

$$\frac{1}{\widehat{\tau}_R} \cong \frac{1}{3\sqrt{\pi}}\frac{Bn_b}{m^{1/2}T^{3/2}} \quad \textit{(provisional)}. \quad (10.51)$$

Note that the collision frequency depends on the number density of the bath, not of the test particles. It should be stressed that the choice of the numerical factor in this formula is somewhat arbitrary: we could have chosen, for instance, to multiply this formula by the factor 75/40 associated with the heat flux. Actually, the various

physical quantities relax with slightly different characteristic times; these all scale like (10.51) with B, n, m, T, but differ by numerical prefactors (of order one). The final choice is a matter of convenience, that will be settled at the end of the calculation.

We also use the following abbreviations for the dimesionless source terms in Eqs. (10.42):

$$g_r^{(1)} = -\widehat{\tau}_R \left(\frac{T}{m}\right)^{1/2} \frac{1}{nT} \nabla_r(nT),$$

$$g_r^{(3)} = -\widehat{\tau}_R \sqrt{\tfrac{5}{2}} \left(\frac{T}{m}\right)^{1/2} \frac{1}{T} \nabla_r T. \tag{10.52}$$

Eqs. (10.42) are now rewritten compactly as:

$$\widehat{\tau}_R \, \partial_t h_r^{(p)} + \sum_{q=1,3} c_{pq} \, h_r^{(q)} = g_r^{(p)}, \quad p = 1, 3. \tag{10.53}$$

The coefficients $c^{(pq)}$ are the *matrix elements of the collision operator* in the Hermite representation:

$$c_{11} = 1, \quad c_{13} = c_{31} = -\frac{3}{2\sqrt{10}}, \quad c_{33} = \frac{75}{40}. \tag{10.54}$$

We note that this matrix is *symmetric*: this follows from a very important property: *The collision operator is a* SELF-ADJOINT *operator*. As a result, its eigenvalues are real; it turns out, moreover, that they are non-positive:

$$r_1 = -0.7922, \quad r_2 = -2.0828. \tag{10.55}$$

Hence, the collision operator produces a monotonous relaxation of the distribution function towards its equilibrium value. This is another aspect of the irreversibility attached to the collisions.

10.5   Derivation of the Transport Equations

Eqs. (10.53) are the final equations determining the two Hermitian moments retained in the present approximation of the expansion (10.34). They are a very simple set of linear ordinary differential equations with constant coefficients. Their solution for given initial values is obtained by standard methods in terms of a propagator:

$$h_r^{(p)}(t) = \sum_{q=1,3} \left[G^{(pq)}(t) \, h_r^{(q)}(0) + \frac{1}{\widehat{\tau}_R} \int_0^t d\theta \, G^{(pq)}(\theta) \, g_r^{(q)}(t - \theta) \right]. \tag{10.56}$$

The matrix elements of the propagator are:

$$G^{(11)}(t) = \frac{1}{r_1 - r_2} \left\{ (c_{11} - r_2) \exp(-r_1 \frac{t}{\hat{\tau}_R}) + (-c_{11} + r_1) \exp(-r_2 \frac{t}{\hat{\tau}_R}) \right\}$$

$$G^{(13)}(t) = G^{(31)}(t) = \frac{c_{13}}{r_1 - r_2} \left\{ \exp(-r_1 \frac{t}{\hat{\tau}_R}) - \exp(-r_2 \frac{t}{\hat{\tau}_R}) \right\},$$

$$G^{(33)}(t) = \frac{1}{r_1 - r_2} \left\{ (-c_{11} + r_1) \exp(-r_1 \frac{t}{\hat{\tau}_R}) + (c_{11} - r_2) \exp(-r_2 \frac{t}{\hat{\tau}_R}) \right\}.$$

$$(10.57)$$

Eq. (10.56) yields the complete solution of the transport problem, i.e., the expressions of the particle flux and of the heat flux in terms of the driving thermodynamic forces, i.e., the pressure gradient and the temperature gradient, respectively. The answer is not, however, of the "expected" type. There are two typically non-classical features in this solution:

a) The value of the vector moments at time t is determined by the whole history of the driving forces $g_r^{(q)}(t - \theta)$. When these expressions are substituted into the energy balance equation (10.22) (for example), we obtain a *non-Markovian equation for the temperature*.

b) The expression of $h^{(p)}(t)$ depends on the initial value $h^{(p)}(0)$. Again, when this is substituted into the hydrodynamical equations, it implies that the solution of the latter requires the knowledge, not only of the initial data for the hydrodynamical quantities, but also of the non-hydrodynamical ones: these are not specified within the framework of hydrodynamics.

The situation is quite analogous to the derivation of the kinetic equation in Sec. 6.1. The role of the correlation function $g_2(1, 2; t)$ is played here by the non-hydrodynamical Hermitian moments, and Eq. (10.56) is analogous to Eq. (6.3). The solution of the difficulty lies again in noting that we are interested here in the evolution on the hydrodynamical time scale τ_H, which is much longer than the relaxation time $\hat{\tau}_R$. The relevant result is thus the *asymptotic form* of Eq. (10.56), obtained for $t \gg \hat{\tau}_R$. [In the same way, we considered in Sec. 6.2 the asymptotic expression of the correlation function for $t \gg \tau_c$ in order to obtain the kinetic equation]. In the present problem we have the additional advantage that the expression of the propagator is known explicitly, and the asymptotic limit can be evaluated exactly.

Following the reasoning of Sec. 6.2, we "Markovianize" the theory by performing the following operations:

- The first term in Eq. (10.56) is set equal to zero. [This step is clearly justified by the exponential decay of the propagator for $t \gg \hat{\tau}_R$, see (10.56)].

- The retardation in the source terms appearing in the integrand of (10.56) is neglected; we thus change $g^{(q)}(t - \theta)$ to $g^{(q)}(t)$. This is justified because the source

terms vary on the hydrodynamical time scale $\tau_H \gg \hat{\tau}_R$; hence their variation is negligible over the time interval $0 < t < \hat{\tau}_R$ where the propagator is effectively different from zero.

- The upper limit of integration is extended to infinity, because the propagator is exponentially small for $t > \hat{\tau}_R$.

We now introduce the following constants:

$$\overline{G}^{(pq)} = \frac{1}{\hat{\tau}_R} \int_0^\infty d\vartheta \, G^{(pq)}(\vartheta) \,. \tag{10.58}$$

The asymptotic (Markovianized) form of Eq. (10.56) is thus:

$$h_r^{(p)}(t) = \sum_{q=1,3} \overline{G}^{(pq)} g_r^{(q)}(t) \,, \quad p = 1, 3 \,. \tag{10.59}$$

In the present problem, the asymptotic result can be checked by an explicit study of Eqs. (10.56), (10.57), which confirms the validity of the three operations described above. Eqs. (10.59) are the final TRANSPORT EQUATIONS in dimensionless form. They establish a *linear relationship between the fluxes* $h_r^{(p)}(t)$ *and the thermodynamic forces* $g_r^{(p)}(t)$; $\overline{G}^{(pq)}$ is called the *transport matrix;* its coefficients are easily calculated from (10.57), (10.58), thus yielding the explicit form:

$$
\begin{aligned}
h_r^{(1)}(t) &= \frac{1}{\Delta} \left[c_{33} \, g_r^{(1)}(t) - c_{13} \, g_r^{(3)}(t) \right] \,, \\
h_r^{(3)}(t) &= \frac{1}{\Delta} \left[-c_{13} \, g_r^{(1)}(t) + c_{11} \, g_r^{(3)}(t) \right] \,,
\end{aligned}
\tag{10.60}
$$

where:

$$\Delta = c_{11}c_{33} - c_{13}^2 = \frac{33}{20} \,. \tag{10.61}$$

Inserting the numerical values (10.54) of the collisional matrix elements, we obtain:

$$
\begin{aligned}
h_r^{(1)}(t) &= \frac{25}{22} g_r^{(1)}(t) + \frac{\sqrt{10}}{11} g_r^{(3)}(t) \,, \\
h_r^{(3)}(t) &= \frac{\sqrt{10}}{11} g_r^{(1)}(t) + \frac{20}{33} g_r^{(3)}(t) \,,
\end{aligned}
\tag{10.62}
$$

We now write the transport equations in dimensional form, using Eqs. (10.38), (10.41), (10.52). The first equation (10.62) thus becomes:

$$\Gamma = -\frac{25}{22}\frac{\widehat{\tau}_R}{m}\,\nabla(nT) - \frac{5}{11}\,n\frac{\widehat{\tau}_R}{m}\,\nabla T.$$

At this point we choose to fix the final value of the relaxation time τ_R (10.51) by including into its definition the factor $25/22$ ($\approx 1.136...$). In other words, the relaxation time is chosen, conventionally, in such a way as to provide the simplest possible expression for the diffusion coefficient. Thus, Eq. (10.51) is replaced by:

$$\frac{1}{\tau_R} = \frac{22}{75\sqrt{\pi}}\frac{Bn_b}{m^{1/2}T^{3/2}}\,. \tag{10.63}$$

The dimensional transport equations take now the simple form:

$$
\begin{aligned}
\Gamma_r &= -\frac{\tau_R}{m}\nabla_r(nT) - \frac{2}{5}n\frac{\tau_R}{m}\nabla_r T\,,\\
q_r &= -\frac{2}{5}T\frac{\tau_R}{m}\nabla_r(nT) - \frac{4}{3}nT\frac{\tau_R}{m}\nabla_r T\,.
\end{aligned}
\tag{10.64}
$$

10.6　Properties of the Transport Coefficients

The transport equations (10.64) relate the fluxes Γ_r, q_r linearly to their conjugate thermodynamic forces, $-\nabla_r(nT)$, $-\nabla_r T$, respectively, through the *transport matrix*, whose elements are the *transport coefficients*. The transport equations are written compactly by using a notation that is usual in nonequilibrium thermodynamics: the fluxes are denoted by J_A, and the thermodynamic forces by X_A, $A = 1, 2$. Thus[5]:

$$
\begin{aligned}
J_1 &= \Gamma, & X_1 &= -\nabla\ln(nT),\\
J_2 &= \frac{1}{T}q, & X_2 &= -\nabla\ln T\,.
\end{aligned}
\tag{10.65}
$$

The transport equations are then written as:

$$J_A = \sum_{B=1,2} L_{AB} X_B\,. \tag{10.66}$$

The coefficients are related as follows to the "usual" transport coefficients:

$$L_{11} = nD\,, \quad L_{22} = \kappa\,, \quad L_{12} = \alpha\,, \quad L_{21} = \alpha'\,, \tag{10.67}$$

---

[5]Note that the fluxes Γ and q/T have the same dimensions.

where D is the *diffusion coefficient*, κ is the *thermal conductivity*, α is the *thermodiffusion coefficient*, and α' the *Dufour coefficient*.

In the special case when the temperature is homogeneous, but there exists a pressure gradient, the first equation (10.66) becomes

$$\Gamma = -\frac{D}{T}\nabla(nT);$$

For our system where the ideal gas equation of state applies, this equation reduces to the familiar *Fick law* governing simple diffusion.

$$\Gamma = -D\,\nabla n\,. \tag{10.68}$$

When the pressure is homogeneous, but there is a non-vanishing temperature gradient, the second equation (10.66) reduces to the well-known *Fourier law* (2.6) describing simple heat conduction:

$$q = -\kappa\,\nabla T\,. \tag{10.69}$$

When both the pressure and the temperature are inhomogeneous, the processes of diffusion and of heat conduction become *coupled*, because the transport matrix contains non-diagonal elements. Thus:

$$\begin{aligned}
\Gamma &= -nD\,\nabla\ln P - \alpha\,\nabla\ln T\,,\\
\frac{q}{T} &= -\alpha'\,\nabla\ln P - \kappa\,\nabla\ln T\,.
\end{aligned} \tag{10.70}$$

Thus, a temperature gradient may produce a particle flux even if the pressure is homogeneous (*thermodiffusion*, or *Soret effect*), whereas a pressure gradient produces a heat flux even in absence of a temperature gradient (*Dufour effect*).

The transport equations determine the reaction of the system to the presence of non-vanishing thermodynamic forces that drive it out of equilibrium. In macroscopic physics the transport equations are simply written down as first approximations to the Taylor expansion of a general functional relationship between fluxes and forces, $J_A = f_A(X_1, X_2)$. It is, however, impossible to determine the values of the transport coefficients within that framework. We proved in the present chapter that statistical dynamics fills this gap. On one hand, it derives the hydrodynamic equations from first principles, i.e. from the dynamics of the underlying molecules. It also provides us with an algorithm that allows us to determine the value and the scaling of the transport coefficients, up to any desired degree of precision. To leading order of approximation (i.e., the simplest non-trivial truncation of the Hermitian moment series) we obtain from Eq. (10.64) the *diffusion coefficient*:

$$D = \frac{T}{m} \tau_R ,$$ (10.71)

and the *thermal conductivity:*

$$\kappa = \frac{4}{3} \frac{nT}{m} \tau_R .$$ (10.72)

Next, we note the remarkable symmetry:

$$L_{12} = L_{21} \quad \Rightarrow \quad \alpha = \alpha' = \frac{2}{5} \frac{nT}{m} \tau_R .$$ (10.73)

This is the expression of the celebrated ONSAGER SYMMETRY PRINCIPLE which states that the transport matrix is a symmetric matrix. Our result constitutes a proof of this principle (for our simple system) from kinetic theory. This type of proof is the simplest and most direct derivation; it is, however, restricted to systems for which a kinetic equation (i.e., a collision term) is known.[6] The property directly responsible for the Onsager symmetry is the symmetry of the collision matrix c_{ij}, Eq. (10.54): this expresses the self-adjoint character of the collision operator, a property that ensures the monotonous approach to equilibrium. It should be noted that the symmetry of the transport matrix depends on the specific choice of fluxes and forces used in the transport equations. If, for instance, the density gradient $\nabla \ln n$ were used in Eqs. (10.70) instead of the pressure gradient $\nabla \ln P$, the Onsager symmetry would be broken. The allowable transformations of fluxes and forces that preserve the Onsager symmetry are discussed in textbooks on non-equilibrium thermodynamics.

Eqs. (10.71)-(10.73) are very general as expressed in terms of the relaxation time; the specific nature of the system enters through the form of the latter. Thus, whereas for a weakly coupled system this quantity is given by Eq. (10.63), the corresponding time for a dilute neutral gas treated by the Boltzmann equation (Chap.7) is (up to a constant):

$$\tau_R^{Bo} = \frac{m^{1/2}}{n_b l_C^2 T^{1/2}} ,$$ (10.74)

(where l_C is the range of the interactions). On the other hand, for a plasma of electrons and singly charged ions, the relaxation time is:

$$\tau_R^{Pl} = \frac{m^{1/2} T^{3/2}}{e^4 n_b \ln \Lambda} ,$$ (10.75)

---

[6]Onsager's original proof, followed by many others, is supposedly more general, but requires additional assumptions about the dynamics of fluctuations, as well as thermodynamic restrictions about the state of the system.

where $\ln \Lambda$ is the Coulomb logarithm, defined in Eq. (8.45): it depends logarithmically (thus, weakly) on the temperature and on the density.

These formulae show that, whereas the dependence of the relaxation time on the mass and on the density is practically the same for all three types of systems, the dependence on the temperature is radically different. Whereas the relaxation time becomes shorter for a dilute gas at high temperatures, it becomes very long for a plasma, and more generally, for a weakly coupled system. This rather counter-intuitive result explains that the behaviour of a fusion plasma can be described, up to a certain point, by the "collisionless" Vlasov equation; the determination of the transport coefficients requires, however, a true kinetic equation (such as the Landau or the Balescu-Lenard equation, or a more sophisticated one, whenever anomalous transport is considered).

10.7 Entropy and Transport

We now establish the link between the quantities describing transport (fluxes and thermodynamic forces) and the entropy, which is the central concept in non-equilibrium thermodynamics. We start from the definition (9.54) for the entropy density, which we rewrite in terms of the local RDF (10.2) in the representation (10.31), using also the explicit form of the constant b (9.50):[7]

$$
\begin{aligned}
ns &= -n \int d\mathbf{c}\, \phi^0(c)\,[1 + \chi(\mathbf{c})] \\
&\times \ln \left\{ \frac{h^3 n}{em^3} \left(\frac{m}{T}\right)^{3/2} \phi^0(c)\,[1 + \chi(\mathbf{c})] \right\}.
\end{aligned}
\tag{10.76}
$$

[In order to be consistent with our convention of measuring temperature in energy units, we also agree to measure entropy in units of k_B: as a result, the factor k_B in (9.54) is incorporated into the definition of s]. Eq. (10.76) can be expanded as follows:

$$
s = s^{[0]} + s^{[1]} + \dots
$$

where $s^{[n]}$ is a functional of order n in the deviation χ. The zeroth order term is:

$$
\begin{aligned}
s^{[0]} &= -\ln\left[\frac{h^3 n}{(2\pi mT)^{3/2}}\right] + 1 + \tfrac{1}{2}\int d\mathbf{c}\,\phi^0(c)\,c^2 \\
&= -\ln\left[\frac{h^3 n}{(2\pi mT)^{3/2}}\right] + \frac{5}{2}.
\end{aligned}
\tag{10.77}
$$

---

[7] Here e is the basis of natural logarithms!

This expression coincides exactly with the local equilibrium expression (9.51) of the entropy per particle. The first order term $s^{[1]}$ is identically zero, because of the constraints (10.33). Thus, up to second order in the deviation from equilibrium, the entropy per particle keeps the same form as in local equilibrium:

$$s(\mathbf{x}, t) \cong s^{[0]}[n(\mathbf{x}, t), T(\mathbf{x}, t)];$$

hence it depends on space and time only through the density and the temperature. This fact is used as a starting point in macroscopic non-equilibrium thermodynamics for the derivation of the entropy balance equation (9.58). Here, we rather derive this equation from kinetic theory.

The total entropy flux Φ_S is defined as:

$$
\begin{aligned}
\Phi_{Sr} &= -n \int d\mathbf{c}\, c_r\, \phi^0(c)\, [1 + \chi(\mathbf{c})] \\
&\quad \times \ln\left\{ \frac{h^3 n}{em^3} \left(\frac{m}{T}\right)^{3/2} \phi^0(c)\, [1 + \chi(\mathbf{c})] \right\} \\
&= \tfrac{1}{2} n \left(\frac{T}{m}\right)^{1/2} \int d\mathbf{c}\, c_r \left\{ c^2 + \ln\left[\frac{h^3 n}{em^3} \left(\frac{m}{T}\right)^{3/2} \right] \right\} \phi^0 \chi
\end{aligned}
$$

This total entropy flux contains (as usual) a convective part and a conductive part. The separation is performed by a calculation similar to the one done for the heat flux in Eq. (10.40), with the result:

$$\Phi_{Sr} = \sqrt{\tfrac{5}{2}} nm \left(\frac{T}{m}\right)^{3/2} h_r^{(3)} + s\, \Gamma_r$$

Thus, the conductive entropy flux (the first term) is simply the heat flux divided by the temperature:

$$\mathbf{J}_S = \frac{\mathbf{q}}{T}. \tag{10.78}$$

We now consider the source term in Eq. (9.58), i.e., the rate of entropy production given by Eq. (9.60) or, using the form (6.34) of the collision term:

$$\sigma(\mathbf{x}, t) = A \int d\mathbf{v}_1 d\mathbf{v}_2 \, [f(\mathbf{v}_1; \mathbf{x}, t) f_b(\mathbf{v}_2; \mathbf{x}, t)]^{-1} \, W_r G_{rs} W_s, \tag{10.79}$$

where the tensor G_{rs} is defined in Eq. (6.31) and:

$$W_r = \left(\frac{\partial}{\partial v_{1r}} - \frac{\partial}{\partial v_{2r}} \right) f(\mathbf{v}_1; \mathbf{x}, t) f_b(\mathbf{v}_2; \mathbf{x}, t).$$

After substitution of the representation (10.31), (10.35), the evaluation of the rate of entropy production is an elementary but tedious calculation, whose result is remarkably simple:

$$\sigma = \frac{n}{\tau_R} \sum_{p=1,3} \sum_{q=1,3} c_{pq}\, h_r^{(p)} h_r^{(q)}\,, \qquad (10.80)$$

where c_{pq} are the matrix elements of the collision operator, Eq. (10.54). The rate of entropy production thus appears as a *quadratic form in the Hermitian moments, whose coefficients are solely determined by the collision term, i.e., the real source of the irreversibility; it is, moreover, proportional to the collision frequency, τ_R^{-1}.* The only assumption underlying Eq. (10.80) is the validity of Eq. (10.35), expressing that the system is not too far from local equilibrium.[8] Eq. (10.80) will be called the *kinetic form of the entropy production rate.*

We now consider the *sign* of this quantity. For the simple case considered here, it is well known from algebra that the criterion for the quadratic form to be definite positive (i.e., $\sigma \geq 0$, for any value of $h_r^{(p)}$) is:

$$c_{11} > 0, \quad c_{33} > 0, \quad c_{11}c_{33} - c_{13}^2 > 0\,. \qquad (10.81)$$

It is immediately checked that the values (10.54), (10.61) satisfy these criteria.

We note that Eq. (10.80), combined with (10.50) can also be written in the form:

$$\sigma = -n \sum_p h_r^{(p)} Q_r^{(p)}\,. \qquad (10.82)$$

The entropy production rate now appears as a bilinear form in the Hermitian moments and the corresponding generalized frictions. The latter can be eliminated by using the linearized equations for the Hermitian moments (10.42), setting $\partial_t h_r^{(p)} = 0$, and using also (10.52):

$$\sigma = \frac{n}{\tau_R} \left[h_r^{(1)} g_r^{(1)} + h_r^{(3)} g_r^{(3)} \right]\,. \qquad (10.83)$$

The remarkable feature appearing at this stage (and which cannot be appreciated from our treatment of a simplified situation) is that Eq. (10.83) is valid as it stands, *whatever the level of truncation of the Hermitian moment series.* In this form, the higher order moments do not contribute to σ (because $g_r^{(p)} \equiv 0$ for $p > 3$)[9]. Thus, the infinite quadratic form (10.80) is cut down to a finite bilinear form in the fluxes

---

[8]When additional irreversible processes (such as viscosity) are considered, and the series (10.34) of Hermite polynomials is truncated at a higher level, the entropy production appears as a quadratic form in the Hermitian moments of all orders and all tensorial natures.

[9]For full generality one must only insert an additional term $h_{rs}^{(2p)} g_{rs}^{(2p)}$ to take account of the viscosity.

and the conjugate thermodynamic forces. When written in terms of dimensional quantities, (10.83) becomes:

$$\begin{aligned}
\sigma &= J_1 X_1 + J_2 X_2 \\
&= -\mathbf{\Gamma} \cdot \nabla \ln P - \frac{1}{T} \mathbf{q} \cdot \nabla \ln T.
\end{aligned} \tag{10.84}$$

~~This well-known~~ form of the entropy production rate as a bilinear form in the fluxes and the thermodynamic forces is derived in the framework of ~~nonequilibrium thermo-~~ dynamics by combining the entropy balance equation with the balance equations of the particle number and of the internal energy. Eqs. (10.83) or (10.84) are therefore called the *thermodynamic form of the entropy production*. The derivation presented here is purely kinetic.

A very interesting feature of the thermodynamic form (10.83) of the entropy production is that its coefficients do not contain any characteristic microscopic parameter. Indeed, the combination $\tau_R^{-1} g_r^{(p)}$ is independent of τ_R. Thus, unlike the kinetic form (10.80), the thermodynamic form is independent of any specific collisional model: this constitutes its generality.

A third interesting form of the entropy production is obtained by substituting the explicit forms of the fluxes given by the transport equations (10.66) into (10.84):

$$\sigma = \sum_A \sum_{B=1,2} L_{AB} X_A X_B. \tag{10.85}$$

This will be called the *transport form of the entropy production*: it is a quadratic form in the thermodynamic forces. The associated matrix L_{AB} is simply the *transport matrix*, i.e., the matrix of the transport coefficients (10.67). Each of these coefficients contributes a term to the entropy production. The definite positive character of the entropy production thus introduces the following constraints on the transport coefficients:

$$D > 0, \quad \kappa > 0, \quad nD\kappa - \alpha^2 > 0. \tag{10.86}$$

The validity of these constraints for our system is immediately checked from Eqs. (10.71) – (10.73). Thus, the second law of thermodynamics requires a positive sign for the diagonal transport coefficients, i.e., the diffusion coefficient D and the thermal conductivity κ. There is, however, no sign requirement for the thermodiffusion coefficient α which may be positive or negative.

10.8   Conclusions

The results presented in the present chapter illustrate the realization of the final practical purpose of "non-equilibrium statistical mechanics". It completes the second part of our work. The program has been realized in two steps, representing the transition through three levels of description:

- *The microscopic level*, described by the phase space distribution function and the Liouville equation or, equivalently, by the infinite set of reduced distribution functions and the BBGKY hierarchy;

- *The kinetic level*, i.e. an "intermediate" reduced microscopic level, described by the one-particle RDF and the asymptotic, irreversible kinetic equations;

- *The macroscopic level*, described in terms of the hydrodynamical fields.

After passing through these steps, the macroscopic description of Sec. 2.2 is recovered from strict Hamiltonian dynamics of a large system, in the asymptotic limit of a long-time description. The transport theory developed here is based on the idea that dissipation is produced by *collisions:* this is indeed the case in the *hydrodynamic regime* defined by the ordering (6.8) which describes a situation where the mean free path is much smaller than any macroscopic length. Many generalizations of this *classical transport theory* can be envisaged: many-component systems, polyatomic molecules, liquids, solids, strong thermodynamic forces, hence nonlinear transport equations, etc. All these questions can be studied within the same framework of a kinetic theory based on the concept of collisions: we do not develop these questions here, but rather refer the reader to the literature.

The classical transport theory is not always applicable. There exist physically realizable conditions where the criterion (6.8) is violated. An important example is provided by a weakly coupled gas (or a plasma) where the collision frequency τ_R^{-1} given by Eq. (10.63) is proportional to $T^{-3/2}$, hence becomes very small at high temperature. In such a weakly collisional regime there exist alternative mechanisms of dissipation which may become dominant under conditions where they are not masked by the collisions. New methods must be developed for the study of such problems: in our terminology, non-equilibrium statistical mechanics must be enlarged to "statistical dynamics". This will be the object of the forthcoming chapters.

10.9   Bibliographical Notes BN10

The first rigorous calculation of the transport coeficients was done by:

Maxwell, J.C., 1867, Phil. Trans. Roy. Soc., **157**, 49.

He discovered an extraordinary property of a special interaction potential $[V(r) = Ar^{-4}]$ that allowed him to calculate these quantities without having to solve a kinetic equation.

This special property of the Maxwell potential was confirmed when Boltzmann derived his equation. Boltzmann himself made some "heroic" attempts to solve his equation, without much success: he became quite discouraged by this failure.

The first sytematic method of solution of the Boltzmann equation is found in:

Hilbert, D., 1912, Math. Annalen, **72**, 562.

The next, very important step was taken independently by:

Chapman, S., 1916, Proc. Roy. Soc. London, **A 93**, 1,

Enskog, D., 1917, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen*, Almqvist and Wiksells, Uppsala.

The most detailed accounts of the calculation of the transport coefficients from the Boltzmann equation are given in the following classical references, using the Chapman-Enskog method:

Chapman, S. and Cowling, T., 1952 (**BN7**),

Hirschfelder et al., 1954 (**BN7**),

and all references quoted in **BN7**, to which we add:

Waldmann, L., 1958, in: *Handbuch der Physik,* (S. Flügge, ed.), vol. 12, Springer, Berlin,

Résibois, P., 1969, Phys. Lett., **A 30**, 465; 1970, J. Stat. Phys., **2**, 21,

Ferziger, J.H. and Kaper, H.G., 1972, *Mathematical Theory of Transport Processes in Gases*, North Holland, Amsterdam.

The method of *Hermitian moments* was first introduced by:

Grad, H., 1949, Commun. Pure Appl. Math., **2**, 311.

A brief account of the history of the calculation of the transport coefficients is given in the bibliographical notes to Chap.13 of **RB-2 (BN1)**.

A more detailed history of transport theory is:

Brush, S.G., 1972, *Kinetic Theory*, vol. 3, Pergamon, Oxford;

This book contains reprints of the english translations of the historical papers by Hilbert, Chapman and Enskog.

The most complete history of kinetic theory is:

Brush, S.G., *The Kind of Motion we call Heat*, 2 volumes; published in the series: *"Studies of Statistical Mechanics"*, vol. 6, (E.W. Montroll and J.L. Lebowitz, eds.), North Holland, Amsterdam.

Among the many authors who calculated the transport coefficients of a plasma using the Landau equation, we quote:

Cohen, R.S., Spitzer, L. and McRoutly, P., 1950, Phys. Rev., **80,** 230,

Braginskii, S.I., 1965, in: *Reviews of Plasma Physics*, (M.A. Leontovich, ed.), vol. 1, Consult. Bur., New York,

Kaneko, S.J.and Yamao, A., 1980, J. Phys. Soc. Japan, **15**, 2098.

The Balescu-Lenard equation was used for calculating transport coefficients by: Gorbunov, L.M. and Silin, V.P., 1964, Zh. Tekhn. Fiz., **34**, 385.

A very extensive treatment of the plasma transport equations (which inspired the treatment given here) is given in **RB-3 (BN1).**

The classical expositions of the questions related to the entropy production and transport are:

Prigogine, I., 1969, *Introduction to Thermodynamics of Irreversible Processes*, Interscience, New York,

de Groot, S.R. and Mazur, P., 1984, *Nonequilibrium Thermodynamics* (reprint), Dover, New York.

See also: **RB-3** for a more recent version, similar to (but more complete than) the one presented here.

Chapter 11

Transport and Autocorrelation Functions

11.1 Introduction

Dissipation is always associated with a certain form of random process. In the problems studied in Chaps. 6 - 10, the "quasi-stochastic" processes driving the dissipation are the individual particle collisions. But the randomness could also be associated with collective phenomena. Typically, some forms of *"waves"* may exist in the system: such waves interact by nonlinear coupling. These interactions may lead to simple decay, generation or transformation processes, but also, under certain conditions, to a chaotic behaviour. In the latter case we reach a *turbulent state* which requires a statistical treatment. Such a chaotic behaviour produces dissipation and provides us with a new mechanism of transport. Turbulent systems can, in principle, be described by appropriate kinetic equations; the treatment of the latter becomes, however, prohibitively complex. For this reason, several different approaches to the transport problem have been devised in order to treat such non-classical regimes: these will be described in the forthcoming chapters of this book. In order to prepare the way, we discuss in the present chapter such an alternative method. In the hydrodynamic regime it yields, of course, the same results as the kinetic method of Chap. 10, but it can be extended rather easily to cover non-classical situations.

11.2 Mean Square Displacement and Diffusion

We treat here, as an illustration, a problem that is slightly more complicated than the one considered in Chap. 10: diffusion of charged particles in presence of a constant magnetic field **B** directed along the z-axis of a cartesian reference frame. For simplicity, we assume that the temperature is constant, but that the particle den-

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sity is spatially inhomogeneous. The number density $n(\mathbf{x}, t)$ of particles obeys the macroscopic continuity equation (10.20).[1] The particle flux is related to the density gradient by Fick's law (10.68). However, the magnetic field introduces a privileged direction; the system is therefore anisotropic and the scalar diffusion coefficient D is replaced by a diffusion tensor D:

$$\boldsymbol{\Gamma}(\mathbf{x}, t) = -D \cdot \nabla n(\mathbf{x}, t).$$ (11.1)

We assume the following form for the diffusion tensor (which will be confirmed by the forthcoming calculation):

$$D = D_\perp (\mathbf{e}_x \mathbf{e}_x + \mathbf{e}_y \mathbf{e}_y) + D_\parallel \mathbf{e}_z \mathbf{e}_z,$$ (11.2)

where $\mathbf{e}_s$ is a unit vector in the s-direction ($s = x, y, z$). This corresponds to a gyrotropic symmetry, i.e. two-dimensional isotropy in the $x - y$ plane perpendicular to B. The transport is thus characterized by two different diffusion coefficients. Assuming that the vector ∇n lies in the $x - z$ plane, we combine Eq. (10.20) with (11.1), (11.2) and obtain the following DIFFUSION EQUATION:

$$\partial_t n(\mathbf{x}, t) = \left(D_\perp \nabla_x^2 + D_\parallel \nabla_z^2 \right) n(\mathbf{x}, t).$$ (11.3)

We now note that $n(\mathbf{x}, t)$ can also be interpreted in a probabilistic way. We consider a system of particles undergoing mutual collisions. Instead of being described dynamically by an interaction Hamiltonian defining a kinetic equation, the collisions are now modelled as producing a random noise. The individual orbits are no longer described deterministically, but rather require a statistical description. It was shown in Sec. 9.2 that, under simple conditions, this philosophy leads to a Fokker-Planck equation, or even to a simple diffusion equation [see Eq. (9.20)]. The function $n(\mathbf{x}, t)$ is then identified with the probability density of finding a particle at point $\mathbf{x}$ at time t (normalized to the constant total number of particles N). We define the MEAN SQUARE DISPLACEMENT ($\langle \delta x^2(t) \rangle$) (briefly: MSD) in the x-direction of a test particle (starting at $\mathbf{x} = 0$ at time $t = 0$ with probability 1) as the value of the square of the displacement from its average position at time t, averaged over an ensemble of realizations characterized by the probability density $n(\mathbf{x}, t)$:

$$\left\langle \delta x^2(t) \right\rangle = \left\langle \left[x(t) - \langle x(t) \rangle \right]^2 \right\rangle = \left\langle x^2(t) \right\rangle - \left\langle x(t) \right\rangle^2.$$ (11.4)

The average position is obtained as follows, by using (11.3):

$$d_t \langle x(t) \rangle = d_t N^{-1} \int d\mathbf{x} \, x \, n = N^{-1} \int d\mathbf{x} \, x \, D_\perp \nabla_x^2 n = 0.$$ (11.5)

---

[1] We omit the species index, which is irrelevant in the present problem.

[The last step is obtained by two integrations by parts over x; it is assumed that both n and ∇n vanish at infinity]. The average position is thus constant; from the given initial condition it thus follows that $\langle x(t) \rangle = 0$ for all times. Next, we determine the MSD, $\langle \delta x^2(t) \rangle = \langle x^2(t) \rangle$ in a similar way:

$$d_t \left\langle \delta x^2(t) \right\rangle = N^{-1} \int dx \, x^2 \, 2D_\perp \nabla_x^2 n = \frac{2D_\perp}{N} \int dx \, n, \qquad (11.6)$$

hence:

$$D_\perp(t) = \frac{1}{2} \frac{d}{dt} \left\langle \delta x^2(t) \right\rangle. \qquad (11.7)$$

A similar formula relates $D_\parallel(t)$ to $\langle \delta z^2(t) \rangle$.

Before continuing we note an apparent inconsistency in Eq. (11.7). The function $D_\perp(t)$ depends explicitly on time, because the MSD is, in most cases, *not* a linear function of time for all times. $D_\perp(t)$ is, however, always a well defined quantity, which will be called the perpendicular RUNNING DIFFUSION COEFFICIENT. It will appear (as shown in the next section) that in all "classical" cases, the MSD grows proportional to t after a long enough time (after a few relaxation times). The "usual" diffusion coefficient (i.e., the coefficient appearing in Fick's law) is then defined as follows:

$$D_\alpha = \lim_{t \to \infty} D_\alpha(t), \quad \alpha = \perp, \parallel. \qquad (11.8)$$

Whenever this limit is finite and positive, the stochastic process is called a *diffusive process*. In some cases, it may happen that the limit is zero (*subdiffusive process*) or infinite (*superdiffusive process*) or inexistent (*oscillatory process*). These very interesting cases will be treated in the final chapters of this book.

These results provide us with two possible ways of determining the diffusion coefficients. In a first approach, one would solve the diffusion equation (11.3) for $n(x, t)$ and then calculate the second moment of this probability distribution by a quadrature. This is not fundamentally different from the method based on a kinetic equation. Alternatively, one would write an equation of motion for a test particle moving under the action of a *random force* representing the collisions. The solution of this stochastic equation allows us to calculate the MSD by averaging the squared displacement over the realizations of the stochastic process. This method will be illustrated in the next section.

Before closing the present section, we introduce two warning statements. In many works (in particular in works based on numerical simulations) a different definition is used for the diffusion coefficient:

$$\overline{D}_\perp = \lim_{t \to \infty} \frac{\langle x^2(t) \rangle}{2t}. \qquad (11.9)$$

Whenever the process is diffusive, the definitions (11.7), (11.8) and (11.8) are equivalent, $\bar{D}_\perp = D_\perp$, but the equality does not hold for a non-diffusive process. Moreover, the argument of the limit does not define a coherent running diffusion coefficient, displaying correctly the properties of the MSD. Consider, indeed, the extreme example of a constant MSD: in this case there is, of course no diffusion at all. Eq. (11.7) yields, for all times, a zero running diffusion coefficient: $D(t) = 0, \forall t$. On the other hand Eq. (11.9) yields $\bar{D}(t) = c/t$, which is non-zero at all times, although it tends asymptotically (very slowly!) to zero.

The second remark concerns the cases where the diffusion coefficients enter Eq. (11.3) depend on the position x. This is often the case in a Fokker-Planck equation (9.19) describing a certain type of spatially inhomogeneous systems. Repeating the calculations (11.5), (11.6) for the case when $D_\perp = D_\perp(\mathbf{x})$, we find a non-vanishing derivative of the first moment:

$$d_t \langle x(t) \rangle = 2 \langle \nabla_x D_\perp(\mathbf{x}) \rangle + \langle x \nabla^2 D_\perp(\mathbf{x}) \rangle. \tag{11.10}$$

Upon calculating the MSD, we must properly subtract the contribution of the non-zero first moment:

$$\begin{aligned}
d_t \langle \delta x^2(t) \rangle &= d_t \left[\langle x^2(t) \rangle - \langle x(t) \rangle^2 \right] \\
&= 2 D_\perp(\mathbf{x}) + 4 \langle x \nabla_x D_\perp(\mathbf{x}) \rangle + \langle x^2 \nabla^2 D_\perp(\mathbf{x}) \rangle \\
&\quad -2 \langle x \rangle \langle \nabla_x D_\perp(\mathbf{x}) \rangle - \langle x \rangle \langle x \nabla^2 D_\perp(\mathbf{x}) \rangle.
\end{aligned} \tag{11.11}$$

Clearly, the simple relation (11.7) between diffusion coefficient and MSD breaks down whenever $D_\perp = D_\perp(\mathbf{x})$.[2] It follows that the second method of determination of the diffusion coefficient, mentioned above and developed in Sec. 11.3, is no longer of any use when this coefficient is x-dependent. It is important to stress this warning because, strangely, it does not seem to be mentioned in the literature, in spite of the widespread use made of the relations (11.7) and (11.9) in numerous works.

11.3   The Langevin Equations

The A-Langevin Equations

We return to the problem defined in the previous section and write the equation of motion of a charged test particle in presence of a constant magnetic field $\mathbf{B} = B e_z$ and undergoing collisions with the particles in the medium. The former acts on the particle via the well-known Lorentz force oriented in a direction perpendicular to B.

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[2]The results (11.5), (11.7) are, of course recovered when $D_\perp(\mathbf{x})$ reduces to a constant.

The collisions are modelled as a force which produces, on the average, a systematic friction proportional to the velocity, but whose instantaneous intensity and direction is random. The Newton equations for the acceleration of the test particle are thus written as:

$$\frac{dv_\perp(t)}{dt} = \Omega\left[v_\perp(t) \times e_z\right] - \nu v_\perp(t) + a_\perp(t)\,, \tag{11.12}$$

$$\frac{dv_z(t)}{dt} = -\nu v_z(t) + a_z(t)\,. \tag{11.13}$$

Here and in forthcoming equations, for any vector $\mathbf{A}$, we denote by $\mathbf{A}_\perp$ the two-component vector (A_x, A_y) perpendicular to the magnetic field. Ω denotes the *Larmor frequency* of a particle of mass m and charge e in the magnetic field of strength B (c is the speed of light; Gaussian units are used for electromagnetic quantities):

$$\Omega = \frac{eB}{mc}\,. \tag{11.14}$$

As explained above, the collisional force has an average component $-m\nu v(t)$ and a random, fluctuating component $ma(t)$. The constant ν (which has the dimension of an inverse time) is identified with the *collision frequency*. In the present philosophy, the function $a(t)$ is not determined: it can only be defined by its statistical properties (see Sec. 9.2). This implies that the object $a(t)$ cannot assume any numerical values. Only its average, or the average of a function of a, has a definite value. It follows that the same property is induced upon the unknown quantity $v(t)$. Thus, Eqs. (11.12), (11.13) are STOCHASTIC DIFFERENTIAL EQUATIONS, that must be treated by methods different from ordinary differential equations, i.e., as will be shown below.

Particularly interesting are averages of products of random quantities (*moments*). Among these, a special importance is attached to the average of a product of a quantity $A(t)$ at time t and the same quantity at a different time t': $\alpha(t, t') = \langle A(t)\,A(t')\rangle$ [the angular brackets denote an average over the ensemble of realizations of the stochastic quantity]. Several equivalent names are given to this expression: the SECOND MOMENT of the random process $A(t)$, or the this is called the TWO-TIME CORRELATION FUNCTION of $A(t)$, or the AUTOCORRELATION FUNCTION of $A(t)$. Any one of these names will be used, for convenience. In order to characterize the stochastic process, we also need to know the n-time correlation functions, i.e., $\langle A(t_1)\,A(t_2)...A(t_n)\rangle$ [see also the discussion of Sec. 9.2]. We may also define time correlations of different random quantities: $\langle A(t_1)\,B(t_2)...N(t_n)\rangle$. These time correlations may be interrelated in a way that depends on the probability distribution of the random function $A(t)$. The simplest situation arises when the distribution of $A(t)$ is a Gaussian with vanishing average, $\langle A(t)\rangle = 0$. In that case, it is well known that all odd moments

of $A(t)$ vanish, and all even order moments are expressed as sums of products of the two-time correlation $\alpha(t, t')$. In other words, a Gaussian process is completely defined by its first two moments. We finally define a STATIONARY STOCHASTIC PROCESS as one for which the autocorrelation function depends only on the difference between the two times: $\alpha(t, t') = \alpha(t - t')$: in this case the relation between two events depends only on the time interval between them, whatever the initial time considered.

We now return to the stochastic differential equation. In order to obtain a definite mathematical object, the random function appearing in it [in our case, the acceleration $a(t)$] must be defined statistically *a priori*: this requires the specification of its probability distribution, considered as a *given* property. The strategy of solution is then as follows. The equation is solved *formally* as an ordinary one: we thus obtain an expression of the unknown $\mathbf{v}(t)$ as a functional of $a(t)$ (which is a source term in the equation). From this expression, the average of any function of $\mathbf{v}$ can be calculated in terms of averages of functions of $a(t)$, whose statistical properties are known.

In our case, we assume that $a(t)$ is a *stationary, delta-correlated Gaussian process (white noise)*. This means that the first and second moments of the acceleration are:

$$\langle a_r(t) \rangle = 0, \qquad \langle a_r(t) a_s(t + \tau) \rangle = A\, \delta_{rs}\, \delta(\tau), \qquad r, s = x, y, z; \qquad (11.15)$$

the constant A will be determined below. The second moment appearing here is the *acceleration autocorrelation function*. Eqs. (11.12), (11.13), completed with (11.15) are characteristic examples of LANGEVIN EQUATIONS, or more specifically: A-Langevin equations (A stands for: "acceleration").[3] The Langevin equations, in turn, are special cases of *Stochastic differential equations*.

The following initial condition is assumed: *the velocity of the test particle has, at time zero, the value* $\mathbf{v}(0) = \mathbf{v}_0$, *with probability* 1. Eqs. (11.12) and (11.13) are solved *for a given realization of the fluctuating acceleration* $a(t)$: the equations are then treated as ordinary differential equations. Their solution is straightforward (details are omitted here) and can easily be checked: it is best expressed in terms of a propagator $G(t)$:

$$\mathbf{v}(t) = G(t) \cdot \mathbf{v}_0 + \int_0^t d\theta\, G(\theta) \cdot a(t - \theta). \qquad (11.16)$$

The propagator is defined by the following matrix:

$$G(t) = \begin{pmatrix} e^{-\nu t}\cos(\Omega t) & e^{-\nu t}\sin(\Omega t) & 0 \\ e^{-\nu t}\sin(\Omega t) & e^{-\nu t}\cos(\Omega t) & 0 \\ 0 & 0 & e^{-\nu t} \end{pmatrix}, \quad t > 0. \qquad (11.17)$$

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[3]The Langevin equation was originally introduced for the study of the Brownian motion of a heavy particle undergoing collisions with the light particles of the surrounding fluid.

This solution represents the well-known motion of the test particle describing a circular helix around a magnetic field line in absence of collisions; the latter produce (on the average) a damping of this motion. As explained above, the velocity $\mathbf{v}(t)$ is a random quantity, just like $\mathbf{a}(t)$: its statistical properties are determined by those of the acceleration. Thus, averaging both sides of Eq. (11.16) over the ensemble of realizations of the fluctuating force and using (11.15), we find:

$$\langle \mathbf{v}(t) \rangle^{(0)} = \mathsf{G}(t) \cdot \mathbf{v}_0. \tag{11.18}$$

(The superscript 0 means that the average is calculated for a given, deterministic initial condition $\mathbf{v}_0$). The *velocity autocorrelation functions*, for $t_1 > t_2$, are obtained as:

$$\boxed{\begin{aligned} R_{xx}^{(0)}(t_1, t_2) &\equiv \langle v_x(t_1) v_x(t_2) \rangle^{(0)} \\ &= \exp[-\nu(t_1 + t_2)] \left[\cos(\Omega t_1) \cos(\Omega t_2) v_{0x}^2 + \sin(\Omega t_1) \sin(\Omega t_2) v_{0y}^2 \right] \\ &\quad + \frac{A}{2\nu} \exp[-\nu(t_1 - t_2)] \left[1 - \exp(-2\nu t_2)\right] \cos[\Omega(t_1 - t_2)] \end{aligned}} \tag{11.19}$$

[The parallel autocorrelation function $R_{zz}^{(0)}$ is obtained by setting $\Omega = 0$ in this formula]. Up to this point we considered the initial velocity as a given, deterministic quantity. The test particle in our problem represents, however, an undistinguished particle, chosen at random among the 10^{23} particles of a plasma, which we may assume to be (at least locally) in thermal equilibrium. We are thus naturally led to complete our problem by *considering the initial velocity $\mathbf{v}_0$ as a random variable, whose probability distribution is Maxwellian:*

$$\varphi(\mathbf{v}_0) = \pi^{-3/2} V_T^{-3} \exp\left(-\frac{v_0^2}{V_T^2}\right), \tag{11.20}$$

where V_T is the *thermal velocity:*

$$V_T = \left(\frac{2T}{m}\right)^{1/2}. \tag{11.21}$$

We now take the point of view that *the physically observable quantities are defined as double averages over both* $\mathbf{a}(t)$ *and* $\mathbf{v}_0$. The doubly averaged velocity, obtained from (11.18) [this quantity is denoted by an overbar], then becomes simply:

$$\overline{\langle \mathbf{v}(t) \rangle} = 0. \tag{11.22}$$

The perpendicular velocity autocorrelation function, averaged over $\mathbf{v}_0$, is:

$$R_{xx}(t_1, t_2) \equiv \overline{\langle v_x(t_1)\, v_x(t_2)\rangle} = \int dv_0\, \varphi(\mathbf{v}_0)\, R_{xx}^{(0)}(t_1, t_2)$$

$$= \frac{1}{2}\left\{\frac{A}{\nu}\, e^{-\nu|t_1 - t_2|} + \left(V_T^2 - \frac{A}{\nu}\right) e^{-\nu(t_1 + t_2)}\right\} \cos[\Omega(t_1 - t_2)],$$

$$t_1 > 0, \quad t_2 > 0. \tag{11.23}$$

Next, we note that this autocorrelation function is not stationary: it depends on both $(t_1 - t_2)$ and $(t_1 + t_2)$ [it is physically unreasonable because nothing in the physical situation allows us to distinguish a privileged time. This difficulty is, however, easily eliminated by using the freedom that is still at our disposal: we choose the value of the constant A in Eq. (11.15) as:

$$A = \nu V_T^2. \tag{11.24}$$

The velocity autocorrelation functions then reduce to the following expressions, which only depend on the difference of the times: $\tau = t_1 - t_2$, and thus describe a stationary process:

$$\boxed{R_{xx}(\tau) = \frac{1}{2}\, V_T^2 \exp[-\nu|\tau|]\, \cos(\Omega\tau)}, \tag{11.25}$$

$$R_{zz}(\tau) = \frac{1}{2}\, V_T^2 \exp[-\nu|\tau|]. \tag{11.26}$$

These functions (scaled with $\frac{1}{2} V_T^2$) are plotted in Fig. 11.1 against the reduced time $\theta = \nu\tau$ [the reduced Larmor frequency is $\omega = \Omega/\nu$].

It will be seen below that their exponential decay is an important feature, ensuring the diffusive character of the process.

The V-Langevin Equations

We now determine the instantaneous position $\mathbf{x}(t)$ of the test particle: this requires the solution of the following equations [4]:

$$\frac{dx(t)}{dt} = v_x(t), \quad \frac{dz(t)}{dt} = v_z(t). \tag{11.27}$$

We may use here Eq. (11.16) in order to define the right hand sides, and go through the same steps as before (solve the equations, then average over $\mathbf{a}(t)$ and $\mathbf{v}_0$...). These steps may, however, be short-circuited by considering Eqs. (11.27) as a new set of Langevin equations. The statistical properties of the velocity have been determined

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[4]Because of the gyrotropy of our problem, the x- and y-coordinates are equivalent. It is therefore sufficient to consider a single perpendicular direction, say x.
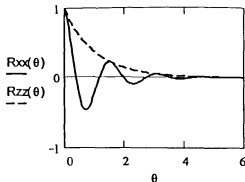
Figure 11.1: Velocity autocorrelations vs. reduced time $\theta = \nu t$. Solid: $R_{xx}(\theta)$ [for $\Omega/\nu = 4$]; Dashed: $R_{zz}(\theta)$.

before. The set (11.27) together with Eqs. (11.22), (11.25) and (11.26) will be called the *V-Langevin equations* of our problem (V stands for "velocity"): they are solved by the same method as the A-Langevin equations. For a given realization of the velocity we obtain:

$$x(t) = x(0) + \int_0^t d\theta \, v_x(\theta) \equiv x(0) + \delta x(t). \qquad (11.28)$$

Eq. (11.22) implies that $\langle x(t) \rangle = x(0)$; thus $\delta x(t)$ represents the instantaneous deviation of the test particle with respect to its average position. We are now ready for the calculation of the mean square displacement (MSD), i.e. the quantity of main interest to us:

$$
\begin{aligned}
\langle \delta x^2(t) \rangle &= \int_0^t d\theta_1 \int_0^t d\theta_2 \, R_{xx}(\theta_1 - \theta_2) \\
&= 2 \int_0^t d\tau \, (t - \tau) \, R_{xx}(\tau).
\end{aligned} \qquad (11.29)
$$

We are now in a position to make contact with the results of the previous section. We obtain the perpendicular running diffusion coefficient by using the definition (11.7):

$$D_\perp(t) = \frac{1}{2} \frac{d}{dt} \langle \delta x^2(t) \rangle = \int_0^t d\tau \, R_{xx}(\tau). \qquad (11.30)$$

Finally, using Eq. (11.8), we obtain the asymptotic diffusion coefficient:

$$D_\perp = \lim_{t\to\infty} D_\perp(t) = \int_0^\infty d\tau \, R_{xx}(\tau) = \int_0^\infty d\tau \, \langle v_x(0) \, v_x(\tau) \rangle \tag{11.31}$$

This is an extremely elegant formula relating the diffusion coefficient (a transport coefficient) to the time integral of the velocity autocorrelation function. In the next section it will appear as a special case of a class of formulae of the same type, that will be derived from statistical mechanics.

We now note that the properties of the velocity autocorrelation function determine the type of transport process going on in the system. If the autocorrelation function ensures the convergence of the integral, the process is *diffusive*: this is the most frequent case met in practice. If the integral in (11.31) diverges, we deal with a *superdiffusive* process. It may also happen that the integral vanishes: we then have a *subdiffusive* process. Note that the latter case requires the velocity autocorrelation to be positive in some domain and negative in the complementary region, and that the areas under these two regions be equal: this is a very delicate condition indeed.

Using now Eq. (11.25), we find the explicit form of the perpendicular running diffusion coefficient:

$$D_\perp(t) = \tfrac{1}{2} V_T^2 \frac{\nu + [\Omega \sin(\Omega t) - \nu \cos(\Omega t)] \exp(-\nu t)}{\nu^2 + \Omega^2}. \tag{11.32}$$

The asymptotic diffusion coefficient is:

$$D_\perp = \lim_{t\to\infty} D_\perp(t) = \tfrac{1}{2} V_T^2 \frac{\nu}{\nu^2 + \Omega^2}. \tag{11.33}$$

The parallel running diffusion coefficient is:

$$D_\parallel(t) = \tfrac{1}{2} V_T^2 \frac{1 - \exp(-\nu t)}{\nu}, \tag{11.34}$$

and the asymptotic parallel diffusion coefficient:

$$D_\parallel = \frac{V_T^2}{2\nu}. \tag{11.35}$$

At this point we have made contact with the results of kinetic theory. Eq. (11.35) is precisely identical to Eq. (10.71) (with $\nu = \tau_R^{-1}$) obtained as a first approximation from the kinetic equation. This result proves the following remarkable fact: *The collision model based on a Gaussian white noise for the fluctuating force is equivalent, in first approximation, to the solution of the kinetic equation in the hydrodynamic regime.* The stochastic treatment based on the Langevin equations is, indeed, completely independent of any kinetic equation; but it cannot provide us with the dependence of the collision frequency on the physical parameters [such as Eq. (10.63)]: ν is here

a free parameter. The previous statement justifies the use of stochastic methods in problems where the kinetic equation becomes prohibitively complicated.

We conclude this section with a discussion of the dependence of the diffusion coefficients on the magnetic field. Clearly, the parallel coefficient is independent of Ω (hence of B): the Lorentz force is zero in the direction of the field. The perpendicular diffusion coefficient is a strongly decreasing function of Ω. In the limit of a very strong magnetic field (i.e.: $\Omega/\nu \gg 1$) it tends to zero like:

$$D_\perp \simeq \frac{V_T^2 \nu}{2\Omega^2}, \quad \Omega/\nu \gg 1 \tag{11.36}$$

This behaviour reflects the fact that the particles spiral around the magnetic field lines: for a very strong field they tend to stick to the field lines. This also explains the different dependence of the diffusion coefficients on the collision frequency. In the parallel direction the collisions hinder the motion of the particles (through friction), hence the diffusion coefficient is inversely proportional to the collision frequency, $D_\parallel \propto \nu^{-1}$. In the perpendicular direction, the particles can move across the (strong) magnetic field only if the collisions decorrelate them from the field lines, hence $D_\perp \propto \nu$. This behaviour, illustrated in Fig. 11.2, is very important for understanding the behaviour of a plasma in a magnetic field.
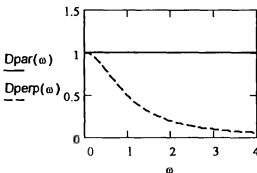

Figure 11.2: Diffusion coefficients (scaled with $D_\parallel$) vs. reduced Larmor frequency $\omega = \Omega/\nu$.

We show in Fig. 11.3 the behaviour of the parallel running diffusion coefficient: starting from zero, it tends exponentially towards its asymptotic constant, positive value. The characteristic time involved is, indeed, the inverse collision frequency. This is the typical *diffusive behaviour* described in the previous section.
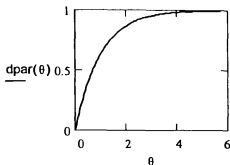
Figure 11.3: Parallel running diffusion coefficient $dpar(\theta) = D_\parallel(\theta)/D_\parallel$, vs. reduced time $\theta = \nu t$.

The perpendicular running diffusion coefficient shown in Fig. 11.4 also tends to an asymptotic positive value; but the behaviour is here oscillatory. In particular, this example shows that nothing prevents the *running* diffusion coefficient from being negative for some limited time.

11.4   The Hybrid Kinetic Equation

We consider the same physical problem as in the previous section, but try to obtain more information. In particular, we ask for the spatial distribution of matter at all times. This question could, in principle be answered by using the Langevin equation: one should then calculate *all* the moments, and then reconstruct from these the instantaneous distribution function. Such a procedure would be very cumbersome and, most often, impracticable. We therefore consider an alternative method, based on an *equation of evolution for a one-particle distribution function*. Instead of providing only the MSD (or some other moments), such an equation yields more global information, such as the shape of the density profile in the system. This equation should describe the action of the two driving forces: the external field B and the collisions. However, *instead of describing the latter by a collision term derived from the exact dynamical interaction potential, as in Chaps. 6 - 10, we adopt here the stochastic modelling of the collisions by a random force*. For this reason, the equations treated in the present section (and later on) will be called HYBRID KINETIC EQUATIONS as they lie in between a dynamical and a stochastic description of the evolution.
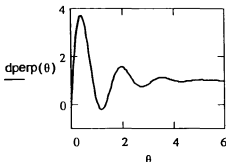
Figure 11.4: Perpendicular running diffusion coefficient (scaled with $D_\perp$); $\omega = 4$.

We thus change, from here on, rather drastically the philosophy of our approach to statistical dynamics. We give up our ambition of deriving macroscopic quantities rigorously from the Hamiltonian dynamics of the particle motion. We rather replace the description of the interactions by a reasonable stochastic model, which allows us to treat more complex problems. We thus accept *"the physicist's compromise"*: either we attempt a mathematically rigorous treatment, but then we can only study oversimplified models of nature; or we want to attack complex realistic systems, but then we must admit some reasonable weaknesses in the physical description.

We illustrate here the procedure in the simplest possible case. We define the distribution function $f(\mathbf{x}; t)$ as the probability density of finding a particle at point $\mathbf{x}$ in physical space, at time t. The hybrid kinetic equation is constructed by using the same idea as in the derivation of the Liouville equation from Hamilton's equations in Chap. 2. The former is a first-order partial differential equation whose characteristic equations are precisely the latter. Using this idea, we construct a *first-order partial differential equation for the distribution function* $f(x; z; t)$ *whose characteristics are the V-Langevin equations* (11.27) [5] *for a given realization of the random velocity* $\mathbf{v}(t)$:

$$\frac{\partial}{\partial t} f(\mathbf{x}; t) + v_x(t) \frac{\partial}{\partial x} f(\mathbf{x}; t) + v_z(t) \frac{\partial}{\partial z} f(\mathbf{x}; t) = 0. \tag{11.37}$$

This equation looks rather different from the usual kinetic equations of statistical

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[5] As explained in the previous section, the gyrotropy of our problem allows us to consider a single perpendicular coordinate. Thus, the vector $\mathbf{x}$ is supposed to be two-dimensional in the present problem: $\mathbf{x} = (x, z)$.

mechanics derived in previous chapters [e.g., (9.62)]. The distribution function appearing here depends only on the spatial coordinates x instead of the complete phase space coordinates (q, v). On the other hand, it contains no (explicit) collision term. This is in accordance with the philosophy of the previous section. The velocity $v(t)$ is considered here as a *given function* of time in any given realization.[6]

In a second step, Eq. (11.37) is to be interpreted as a *stochastic equation*, because the velocity $v(t)$ is considered as a Gaussian stationary random process, defined statistically by Eqs. (11.25), (11.26) which we rewrite here for convenience:

$$\begin{aligned}
\langle v_x(t)\, v_x(t+\tau)\rangle &= \tfrac{1}{2}V_T^2 \exp(-\nu|\tau|)\cos(\Omega\tau), \\
\langle v_z(t)\, v_z(t+\tau)\rangle &= \tfrac{1}{2}V_T^2 \exp(-\nu|\tau|), \\
\langle v_x(t)\, v_z(t+\tau)\rangle &= 0.
\end{aligned} \qquad (11.38)$$

The distribution function $f(x; t)$ thereby becomes a random quantity, whose statistics is induced by the statistics of the velocity (which, in turn, is determined by the collision model). The stochastic equation (11.37), combined with (11.38) will be called the *Hybrid Kinetic Equation* of our problem. The strategy of solution is now straightforward. The hybrid kinetic equation is integrated exactly for a given realization of the velocity; this solution is used for the calculation of the particle flux. The final result is then averaged over v. *This operation does not require any additional probabilistic assumption beyond those underlying the V-Langevin equations.*

We now introduce the following representation of the distribution function:

$$f(x, z; t) = n(x; t) + \delta f(x, z; t), \qquad (11.39)$$

where $n(x; t) = \langle f(x, z; t)\rangle$ is the ensemble-averaged distribution function and $\delta f(x, z; t)$ is the *fluctuation*, whose average is obviously zero: $\langle \delta f\rangle = 0$. It is assumed here that the average distribution function only depends on x (i.e., that the density gradient is perpendicular to the magnetic field). The hybrid kinetic equation is accordingly split into two coupled equations for n and δf. The equation for the former is obtained by ensemble-averaging Eq. (11.37) and integrating over z [7]:

$$\frac{\partial}{\partial t} n(x; t) + \frac{\partial}{\partial x}\,\langle v_x(t)\, \delta f(x, z; t)\rangle = 0. \qquad (11.40)$$

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[6] One could also construct a hybrid kinetic equation associated with the A-Langevin equation (11.12), (11.13). In this case the unknown is a distribution function $f(x, v, t)$ of the position and of the velocity. In the hybrid kinetic equation, however, the acceleration $a(t)$ is now defined statistically by Eq. (11.15) rather than dynamically by an interaction force exerted by the particles of the medium.

[7] The term $\frac{\partial}{\partial z}\langle v_z(t)\delta f(x, z; t)\rangle$ vanishes after averaging over the irrelevant z-coordinate. It may actually be checked a posteriori that the average appearing here is independent of z.

The equation for the fluctuation is obtained by subtracting (11.40) (before the z-integration) from (11.37):

$$\partial_t \delta f + \underbrace{v_x(t)\frac{\partial}{\partial x}\delta f - \left\langle v_x(t)\frac{\partial}{\partial x}\delta f\right\rangle}_{\mathcal{E}^2 + \mathcal{E}^2} + \underbrace{v_z(t)\frac{\partial}{\partial z}\delta f - \left\langle v_z(t)\frac{\partial}{\partial z}\delta f\right\rangle}_{\mathcal{E}^2 + \mathcal{E}^2} = -v_x(t)\frac{\partial}{\partial x}n. \tag{11.41}$$

We now note that Eq. (11.40) has precisely the form (10.20) of the macroscopic continuity equation. We thus identify the (average) particle flux in the x-direction as:

$$\Gamma_x = \langle v_x(t)\delta f(x,t)\rangle. \tag{11.42}$$

Anticipating a check *a posteriori*, we note that the two bracketted terms in (11.41) do not contribute to the particle flux; hence to the average kinetic equation (11.40); the equation for the fluctuations is thus simplified to:

$$\partial_t \delta f + v_x(t)\frac{\partial}{\partial x}\delta f + v_z(t)\frac{\partial}{\partial z}\delta f = -v_x(t)\frac{\partial}{\partial x}n. \tag{11.43}$$

This is formally a linear, first-order, inhomogeneous partial differential equation for δf in any given realization. (It is, however, "stochastically nonlinear".) The propagator of this equation is easily obtained by the method of characteristics:

$$G(x,z,t|x',z',t') = \delta[x - x' - F_x(t,t')]\,\delta[z - z' - F_z(t,t')], \tag{11.44}$$

where $F_i(t,t')$ are obtained from the solution of the V-Langevin equations (11.27):

$$F_i(t,t') = \int_{t'}^{t} d\theta\, v_i(\theta), \quad i = x,z. \tag{11.45}$$

The solution of (11.43) is then:

$$\delta f(x,z;t) = \int dx'dz'\, \{G(x,z,t|x',z',0)\delta f(x',z';0)$$
$$-\int_0^t d\tau\, G(x,z,t|x',z',\tau)v_x(\tau)\frac{\partial}{\partial x}n(x';\tau)\}. \tag{11.46}$$

The first term goes rapidly to zero for a well-localized initial condition, and will be neglected. The second term is easily integrated over x', z'; the result is then substituted into (11.40):

$$\partial_t n(x;t) = \frac{\partial}{\partial x}\int_0^t d\tau \left\langle v_x(t)v_x(\tau)\frac{\partial}{\partial x}n[x - F_x(t,\tau);\tau]\right\rangle. \tag{11.47}$$

This is the exact equation of evolution of the density profile following from the hybrid kinetic equation or - equivalently - from the V-Langevin equations. It is rather surprising to note that the almost trivially simple V-Langevin equations (11.27) lead to such a complicated equation. The most serious difficulty comes from the displacement of the x variable in the right hand side; indeed, the argument F_x is a linear functional of the *random* variable v_x. As a result the integrand is the average of an unknown function $(n[...])$ of v_x! To make sense of this expression, we Taylor expand it as follows:

$$\langle ... \rangle = \langle v_x(t) v_x(\tau) \rangle \frac{\partial}{\partial x} n(x; \tau)$$

$$+ \int d\theta_1 \int d\theta_2 \; \langle v_x(t) v_x(\tau) v_x(\theta_1) v_x(\theta_2) \rangle \frac{\partial^3}{\partial x^3} n(x; \tau) + ... \quad (11.48)$$

Thus, Eq. (11.47) is equivalent to a partial differential equation of infinite order. The coefficients of the successive derivatives involve velocity moments of increasingly high order. Considering the last term in (11.48), we note that, for a Gaussian process, the fourth order moment is a sum of products of two second order moments. Because of the exponential form of the velocity autocorrelations (11.38), the higher moments decrease much faster than the second moment. We may thus simplify the equation of evolution by making the QUASILINEAR APPROXIMATION: all velocity moments of order higher than 2 are neglected; keeping only the first term in (11.48), we obtain:

$$\boxed{\partial_t n(x; t) = \frac{\partial}{\partial x} \int_0^t d\tau \; R_{xx}(\tau) \frac{\partial}{\partial x} n(x; t - \tau).} \quad (11.49)$$

[Here we reverted to the notation R_{xx} (11.23) for the velocity time correlation, and changed the integration variable: $\tau \to t - \tau$.] This looks "almost" like a diffusion equation, except for a major difference: it is a *non-Markovian* diffusion equation. Indeed, the rate of change of $n(x; t)$ at time t depends on the past values of the density profile. We are faced with the same problem as in kinetic theory (Sec. 6.1) and in transport theory (Sec. 10.5). The solution of the difficulty is obtained by a similar reasoning. The velocity correlation decays exponentially with a characteristic time equal to the collisional relaxation time $\boxed{\tau_R = \nu^{-1}.}$ On the other hand, the density profile varies very little over such a time. We are thus justified in introducing asymptotically, for $t \gg \nu^{-1}$ the MARKOVIAN APPROXIMATION:

i) the retardation is neglected in the right hand side: $n(x; t - \tau) \approx n(x; t)$;

ii) the upper limit of integration is extended to infinity.

The resulting equation of evolution for the density profile is then:

$$\partial_t n(x; t) = \frac{\partial}{\partial x} D \frac{\partial}{\partial x} n(x; t), \quad (11.50)$$

This is an *ordinary diffusion equation*, with a constant diffusion coefficient:

$$D = \int_0^\infty d\tau \, R_{xx}(\tau) \tag{11.51}$$

Not surprisingly, we recovered once more the expression (11.30) which was obtained from the V-Langevin equation.[8]

The matter treated in the present section is interesting for several reasons:

- It shows that the hybrid kinetic equation is a useful concept for the study of stochastic processes. In particular, it allows us to obtain directly the density profile by solving the equation for $n(x; t)$.

- It shows that even the derivation of the simplest diffusion equation poses non-trivial problems which are clearly displayed in the hybrid kinetic equation formalism.

- The hybrid kinetic equation will appear as an ideal tool for the study of situations where the assumptions necessary for the diffusion equation are no longer satisfied. This will open the door for the so-called *strange transport* problems that will be discussed in the final chapters of this book.

11.5 The Green-Kubo Formulae

We now show that the relation between transport coefficients and time correlation functions rests on a very general basis and can be derived directly from the Liouville equation. The proof is simplest and clearest in the case of the so-called *mechanical transport coefficients*, which describe the reaction of the system to a perturbation of its Hamiltonian: a typical example is the electrical conductivity. In contrast, the *thermal transport coefficients* are related to the spatial inhomogeneity of the system: they were considered in Chap. 10 and in the previous sections of the present chapter.

We consider a system consisting of N charged particles of several species (particle j bearing the charge e_j). The "internal" Liouvillian is of the standard form describing a system of interacting particles, as given by Eqs. (3.21) - (3.23):

$$L = L^0 + L'. \tag{11.52}$$

We now consider that the system has been left to itself for a long time in the past, so that at time zero it has reached thermal equilibrium. Its phase space distribution is then the canonical equilibrium distribution (3.27):

---

[8]*Had we not implemented the approximation ii) above, we would have obtained a diffusion equation with a time-dependent diffusion coefficient, which is none other than the running diffusion coefficient $D(t)$. We know, of course, that the latter tends exponentially to the constant D.*

$$F(x_1, ..., x_N; 0) = F^0(x_1, ..., x_N) = (N!h^{3N}Z)^{-1} \exp[-\beta H(x_1, ..., x_N)] \qquad (11.53)$$

[We use here the notation (4.1) for the phase space co-ordinates; $\beta = T^{-1}$ is the usual statistical mechanical notation for the inverse temperature in energy units.] At time zero, an external electric field E is switched on (but no magnetic field, for simplicity), that is assumed constant for $t > 0$. For $t > 0$ the Liouvillian thus contains an additional term L^E [see Eq. (3.24)] written explicitly as:

$$L^E = -\sum_{j=1}^{N} e_j E \cdot (\partial/\partial \mathbf{p}_j). \qquad (11.54)$$

We now solve the Liouville equation:

$$\partial_t F = (L + L^E)F, \qquad (11.55)$$

by assuming that L^E is a small perturbation: this is because we are interested in deriving a *linear* transport equation of the form (10.66) between the electric current (flux, J) and the electric field (thermodynamic force, X). The solution is expressed in terms of the propagator $W(t)$ associated with Eq. (11.55):

$$F(t) = W(t) F^0, \qquad (11.56)$$

where $W(t)$ obeys the equation:

$$\partial_t W(t) = LW(t) + L^E W(t), \qquad (11.57)$$

with the initial condition $W(0) = I$. We denote by $U(t)$ the unperturbed propagator obeying:

$$\partial_t U(t) = LU(t), \qquad (11.58)$$

with the same initial condition. Treating the last term in (11.57) as a source term, we obtain the formal "solution":

$$W(t) = U(t) + \int_0^t d\tau \, U(\tau) \, L^E \, W(t - \tau). \qquad (11.59)$$

This is a linear integral equation for the propagator $W(t)$. The approximation to the solution (11.56) is obtained by the first iteration of (11.59), i.e. by the replacement $W(t) \to U(t)$ in the integral; thus:

$$F(t) = U(t)F^0 + \int_0^t d\tau \, U(\tau) \, L^E \, U(t - \tau) \, F^0. \qquad (11.60)$$

We now note that the equilibrium distribution F^0 is a stationary solution of the unperturbed Liouville equation; thus $U(t)F^0 = F^0$, hence:

$$F(t) = F^0 + \int_0^t d\tau \, U(\tau) \, L^E \, F^0. \tag{11.61}$$

We now calculate the ensemble average of the electric current, which is defined microscopically as:

$$\mathbf{j}_e = \sum_{n=1}^{N} e_n \mathbf{v}_n, \tag{11.62}$$

thus:

$$\mathbf{J}_e(t) = \int d^N x \, \mathbf{j}_e \, F(t) \tag{11.63}$$

We note that in equilibrium the average electric current is zero (because $\mathbf{j}_e$ is an odd function of the velocities). Hence, the presence of an average nonvanishing current is a measure of the deviation from equilibrium:

$$\mathbf{J}_e(t) = \int_0^t d\tau \int d^N x \, \mathbf{j}_e \, U(\tau) \, L^E \, F^0 \tag{11.64}$$

From Eqs. (11.53) and (11.54) we obtain:

$$
\begin{aligned}
L^E F^0 &= -\sum_j e_j \mathbf{E} \cdot (\partial/\partial \mathbf{v}_j) F^0 \\
&= \beta \sum_j e_j \mathbf{v}_j \cdot \mathbf{E} \, F^0 = \beta \mathbf{E} \cdot \mathbf{j}_e \, F^0;
\end{aligned}
$$

hence:

$$
\begin{aligned}
\mathbf{J}_e(t) &= \beta \mathbf{E} \cdot \int_0^t d\tau \int d^N x \, \mathbf{j}_e \, e^{\tau L} \left[\mathbf{j}_e F^0 \right] \\
&= \beta \mathbf{E} \cdot \int_0^t d\tau \int d^N x \, F^0 \, \mathbf{j}_e \, e^{-\tau L} \mathbf{j}_e \\
&= \beta \mathbf{E} \cdot \int_0^t d\tau \int d^N x \, F^0 \, \mathbf{j}_e \, \mathbf{j}_e(\tau) \tag{11.65}
\end{aligned}
$$

In the second step we went over to the Heisenberg picture [see the passage from (3.14) to (3.11)] and introduced the time-dependent dynamical function $\mathbf{j}_e(\tau)$. We now recognize in the right hand side an autocorrelation function averaged over the equilibrium distribution function. On the other hand, Eq. (11.65) has precisely the form of a linear transport equation:

$$\mathbf{J}_e(t) = \Sigma(t) \cdot \mathbf{E}, \tag{11.66}$$

where $\Sigma(t)$ is a *running electrical conductivity tensor*:

$$\Sigma(t) = \beta \int_0^t d\tau \, \langle \dot{\mathbf{j}}_e \dot{\mathbf{j}}_e(\tau) \rangle. \qquad (11.67)$$

(We reverted here to the notation of the previous section for the autocorrelation functions.) If the process is diffusive, this quantity tends asymptotically to the "usual" *electrical conductivity tensor*:

$$\Sigma = \lim_{t \to \infty} \Sigma(t) = \beta \int_0^\infty d\tau \, \langle \dot{\mathbf{j}}_e \dot{\mathbf{j}}_e(\tau) \rangle. \qquad (11.68)$$

We thus obtained a relation between the electrical conductivity (a transport coefficient) and the autocorrelation function of the microscopic electric current: this is called a GREEN-KUBO FORMULA after the names of M. Green and R. Kubo who derived (independently) this type of formulae. We now recognize that the expression found in Eq. (11.31) from a Langevin equation treatment has exactly the same structure as (11.68). Actually, considering a system of heavy, immobile ions and current-carrying electrons, we find from the definition (11.62) the following simple relation between electrical conductivity and electron diffusion coefficient:

$$\Sigma = \frac{e^2 n}{T} D. \qquad (11.69)$$

[Here $\Sigma = \frac{1}{3} Tr \, \Sigma$, and D is the scalar diffusion coefficient in absence of a magnetic field, identical to $D_\parallel$ in (11.35)].

The derivation of the electrical conductivity can be generalized to any other mechanical transport coefficient describing the response to a non-equilibrium situation produced by a perturbation of the Hamiltonian. The case of the thermal transport coefficients is not as easily demonstrated. The most convincing proof was given by H. Mori in 1958. In order to introduce the effect of the spatial inhomogeneity, he assumes that the initial state in Eq. (11.56) is a *local equilibrium state* rather than the global equilibrium (11.53). From here on the derivation is rather similar to the previous one. It must be said, however, that the local equilibrium is a clear concept in the context of the kinetic equations, hence of the reduced distribution functions [see (9.63)]; but its extension to the complete phase space is a rather daring generalization. If this type of assumptions is accepted, Mori proved that any thermal transport coefficient can be represented as the time-integral of an autocorrelation function of the corresponding microscopic fluxes. Thus, for instance, the thermal conductivity tensor κ is given by the following Green-Kubo formula:

$$\kappa = (T^2 V)^{-1} \int_0^\infty d\tau \, \langle \dot{\mathbf{j}}_{\text{th}} \dot{\mathbf{j}}_{\text{th}}(\tau) \rangle. \qquad (11.70)$$

(where V is the volume). The definition of the microscopic heat fluxes would be $\sum \frac{1}{2} m v^2 \mathbf{v}$ in the simple cases; however, in the general case treated here one must add

a rather complicated contribution of the interaction energy to the energy flux. We do not further develop this question here.

The Green-Kubo theory is important from a fundamental point of view, because it gives a very general derivation of the transport coefficients from first principles. A very detailed and general theory can be constructed for the properties of the correlation functions (symmetries, consequences of the causality principle, sum rules, dissipation-fluctuation theorem,...). We do not develop these matters here, because we shall not make any further use of this general formalism (the reader is referred to the works cited in BN11). The explicit evaluation of the Green-Kubo formulae is, unfortunately, prohibitive, because they are expressed in the complete phase space, and thus require a treatment of the N-body problem. The practical calculation of the transport coefficients thus will always be done by a reduction of the problem to a kinetic and hydrodynamic limit, as in Chap. 10, or by a stochastic method such as the Langevin equation or the hybrid kinetic equation described in the previous sections.

Before closing this section, we briefly mention a difficulty which was discovered in numerical simulations in 1968, and was the object of a long debate in subsequent works. It appeared that the velocity autocorrelation function of a system of hard spheres has a definitely non-exponential behaviour: for long times it decays slowly as a power law: $t^{-d/2}$ (where d is the dimensionality). It was found afterwards that this *"long tail"* behaviour is predicted by the kinetic equation for moderately dense gases and is related to the non-analyticity of the transport coefficients (see BN7). It finally appeared as a general, unavoidable property of fluids, due to the existence of long wave-length, low frequency hydrodynamic modes. We have no space for a discussion of these problems here, but wish to stress that a similar behaviour will be illustrated in Chap. 12 in connection with the Continuous Time Random Walk. It will be shown that this behaviour implies a strongly non-Markovian evolution.

11.6 Bibliographical Notes BN11

The theory of *stochastic processes*, including the *stochastic differential equations*, is developed in all the references quoted in BN9. The *Langevin equation* was first derived in connection with the theory of Brownian motion in:

Langevin, P., 1908, C.R. Acad. Sciences Paris, **146**, 530.

Specific, non-standard applications of the *Langevin equations* to diffusion in turbulent plasmas are found in:

Balescu, R., Wang, H.-D. and Misguich, J.H., 1994, Phys. Plasmas, **1**, 3826,

Wang, H.-D., Vlad, M., Vanden Eijnden, E., Spineanu, F., Misguich, J. and Balescu, R., 1995, Phys. Rev., **E 51**, 4844,

Vanden Eijnden, E. and Balescu, R., 1995, J. Plasma Phys., **54**, 185; 1996, Phys. Plasmas, **3**, 874.

The problems raised by a *space-dependent diffusion coefficient* was considered in:
Vanden Eijnden, E. and Balescu, R., 1996, Phys. Plasmas, **3**, 815.

The concept of a *hybrid kinetic equation* was introduced in:
Balescu, R., Wang, H.-D. and Misguich, J.H., 1994 (see above)

The expression of the *transport coefficients* in terms of autocorrelation functions was derived, for mechanical coefficients, by:
Green, M.S., 1951, J. Chem. Phys., **19**, 1036,
Kubo, R., 1957, J. Phys. Soc. Japan, **12**, 570.

The theory of *thermal transport coefficients* was given in:
Mori, H., 1958, Phys. Rev., **112**, 1829;   see also:
McLennan, J.A., 1960, Phys. Fluids, **3**, 493,
Jackson, J.L. and Mazur, P., 1964, Physica, **30**, 2295,
Kadanoff, L.P. and Martin, P.C., 1963, Ann. Phys. (NY), **24**, 419.

The *equivalence* between the autocorrelation function method and the kinetic equation method was proved in full generality by:
Résibois, P., 1964, J. Chem. Phys., **41**, 2979.

A very good exposition is given in the book of R. Kubo et al., 1994 (BN3), where many additional references are given. The most complete, very clear and extensive exposition, including both a detailed theoretical exposition and a wealth of experimental data is:
Boon, J.P. and Yip, S., 1980, *Molecular Hydrodynamics*, McGraw Hill, New York; reprinted by Dover, New York (1991).   See also:
Balescu, R., 1975 RB-2 (BN1),
Résibois, P. and De Leener, 1977 (BN7),
McLennan, J.A., 1989 (BN3),
Forster, D., 1990, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions*, Addison Wesley, New York.

The *long tails* in the autocorrelation functions were discovered by:
Alder, B.J. and Wainwright, T.E., 1968, J. Phys. Soc. Japan (Suppl.), **26**, 267; 1969, Phys. Rev. Lett., **18**, 988.

Their kinetic theory was developed by:
Dorfman, J.R. and Cohen, E.G.D., 1970, Phys. Rev. Lett., **25**, 1257,
Ernst, M.H., Hauge, E.H. and van Leeuwen, J.M., 1970, Phys. Rev. Lett., **25**, 1254, 1971, Phys. Rev., A **4**, 2055,
Pomeau, Y., 1968, Phys. Lett., **27**A, 601.

Chapter 12

Random Walks and Transport

12.1 Classical Random Walks

We now go one step further in modelling the transport processes. In complex problems, involving motion of particles through strongly inhomogeneous, partially disordered or turbulent media, even the Langevin or the hybrid kinetic equation approaches could become prohibitive. In such cases a more radical modelling could be useful. The description of the motion by "semi-deterministic" laws (i.e., a Newton equation with random forces) is abandoned; rather, the evolution is described by a set of displacements ruled by purely probabilistic prescriptions. This method has been applied to a large variety of problems, and has been revived in recent years by very important new developments.

We start with the consideration of the very old problem of the RANDOM WALK of a *particle in a d-dimensional space* (the role of dimensionality in these problems is often non-trivial). In its classical version the random walk is a *discontinuous process*: there exists a "quantum" of time τ. Imagine a metronome oscillating with a period τ. At every beat of the metronome (i.e., at each time $t = \nu\tau$), the particle performs a *jump* described by a vector $\mathbf{r}$ of arbitrary length and arbitrary direction. It is assumed that these jumps are statistically independent of each other. The *transition probability density, or probability distribution function (PDF) of a jump* described by a vector $\mathbf{r}$ is denoted by $f(\mathbf{r})$: it is a prescribed function, characteristic of the problem.

Let $n_\nu(\mathbf{x})$ be the *probability density (PDF) of finding the particle at $\mathbf{x}$ after ν steps, knowing that it started certainly in $\mathbf{x} = 0$ at time $t = 0$*: $n_0(\mathbf{x}) = \delta(\mathbf{x})$. Because of the mutual independence of the jumps, an equation for $n_\nu(\mathbf{x})$ is easily established. Indeed, the PDF of finding the particle in $\mathbf{x}$ at time $\nu + 1$ equals the PDF of being in $\mathbf{x}'$ at time ν, times the probability of a jump $(\mathbf{x} - \mathbf{x}')$, summed over all intermediate positions $\mathbf{x}'$:

$$n_{\nu+1}(\mathbf{x}) = \int d^d x' \, f(\mathbf{x} - \mathbf{x}') \, n_\nu(\mathbf{x}').$$ (12.1)

This recurrence relation is very easily solved. Being in the form of a convolution, it is naturally treated by a Fourier transformation. The Fourier transform $\tilde{n}_\nu(\mathbf{k})$ of a PDF is called its *characteristic function*. The characteristic function of the *transition probability* $\tilde{f}(\mathbf{k})$ is called the *structure function* of the random walk. These quantities are defined as follows[1]:

$$\left\{ \begin{array}{c} \tilde{n}_\nu(\mathbf{k}) \\ \tilde{f}(\mathbf{k}) \end{array} \right\} = \int d^d k \, e^{i\mathbf{k}\cdot\mathbf{x}} \left\{ \begin{array}{c} n_\nu(\mathbf{x}) \\ f(\mathbf{x}) \end{array} \right\}.$$ (12.2)

Before continuing, we derive some simple, but very important properties of the characteristic functions. Let $n(\mathbf{x})$ be any PDF, normalized to one, and denote by $\tilde{n}(\mathbf{k})$ its characteristic function. Eq. (12.2) can also be interpreted as an average:

$$\tilde{n}(\mathbf{k}) = \left\langle e^{i\mathbf{k}\cdot\mathbf{x}} \right\rangle$$ (12.3)

From here we obtain the following relations, relating the *moments* of the PDF to the derivatives of its characteristic function, evaluated at $\mathbf{k} = 0$. The normalization condition determines the value of the characteristic function at the origin:

$$1 = \tilde{n}(\mathbf{k} = 0)$$ (12.4)

The average position is obtained as follows:

$$\langle \mathbf{x} \rangle = -i \left. \frac{\partial}{\partial \mathbf{k}} \tilde{n}(\mathbf{k}) \right|_{\mathbf{k}=0}.$$ (12.5)

More generally, for an arbitrary moment, i.e. the average of a product of p components of $\mathbf{x}$ we find:

$$\left\langle x_{a_1} x_{a_2} ... x_{a_p} \right\rangle = i^{-p} \left. \frac{\partial^p}{\partial k_{a_1} \partial k_{a_2} ... \partial k_{a_p}} \tilde{n}(\mathbf{k}) \right|_{\mathbf{k}=0}.$$ (12.6)

Of special importance is the *mean square displacement* (MSD), i.e. the average of the squared distance (in d dimensions) $r^2 = \sum_{i=1}^{d} x_i^2$:

$$\boxed{\left\langle r^2 \right\rangle = -\left. \frac{\partial}{\partial \mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{k}} \tilde{n}(\mathbf{k}) \right|_{\mathbf{k}=0}}$$ (12.7)

---

[1] It may be noted that the definition of the Fourier transform in the context of random walks is slightly different than our usual convention (2.30), (2.31). The factor $(2\pi)^{-d}$ is attached here to the k-integral, rather than to the x-integral. Both conventions are, indeed, correct and equivalent. The present choice yields more "natural" formulae in this problem, such as the expression (12.3) or the normalization condition (12.4), which would otherwise carry inelegant 2π-factors.

We now return to Eq. (12.1) which, upon Fourier transformation becomes:

$$\tilde{n}_{\nu+1}(\mathbf{k}) = \tilde{f}(\mathbf{k})\,\tilde{n}_{\nu}(\mathbf{k}), \qquad (12.8)$$

with the initial condition: $\tilde{n}_0(\mathbf{k}) = 1$. We then find: $\tilde{n}_1(\mathbf{k}) = \tilde{f}(\mathbf{k})$, $\tilde{n}_2(\mathbf{k}) = \tilde{f}(\mathbf{k})\,\tilde{f}(\mathbf{k})$, and in general:

$$\tilde{n}_{\nu}(\mathbf{k}) = \left[\tilde{f}(\mathbf{k})\right]^{\nu}, \qquad (12.9)$$

and, finally:

$$n_{\nu}(\mathbf{x}) = (2\pi)^{-d}\int d^d k\, e^{-i\mathbf{k}\cdot\mathbf{x}}\left[\tilde{f}(\mathbf{k})\right]^{\nu}. \qquad (12.10)$$

This is the complete solution of the classical random walk problem. Clearly, the shape of the density profile will be entirely determined by the structure function $\tilde{f}(\mathbf{k})$.

For simplicity, we first consider only *symmetric random walks*, characterized by even functions of x: $n(\mathbf{x}) = n(|\mathbf{x}|)$, and $\tilde{f}(\mathbf{k}) = \tilde{f}(\mathbf{k})$. An important class of solutions obtains when the structure function corresponds to a so-called *stable distribution*. These distributions are defined by the following invariance property:

$$\tilde{f}(a_1\mathbf{k})\,\tilde{f}(a_2\mathbf{k}) = \tilde{f}(a\mathbf{k}), \qquad (12.11)$$

where a_1, a_2 are given positive constants and a is a function of the latter. The properties of these functions are briefly reviewed in the Appendix. It is shown there that the solutions of this functional equation are the LEVY DISTRIBUTIONS:

$$\tilde{f}(\mathbf{k}) = \exp\left(-C\,|\mathbf{k}|^{\beta}\right), \quad 0 < \beta \leq 2. \qquad (12.12)$$

(The limitation is due to the fact that for $\beta > 2$ the transition PDF $f(\mathbf{x})$ is no longer positive definite.) Some useful properties of the Lévy distributions are collected in the Appendix. Eq. (12.11) is generalized as follows:

$$\prod_{m=1}^{j}\tilde{f}(a_m\mathbf{k}) = \tilde{f}(a\mathbf{k}) \qquad (12.13)$$

with the composition law (for the Lévy distribution):

$$a = \left(\sum_{m=1}^{j} a_m^{\beta}\right)^{1/\beta} \qquad (12.14)$$

We find, in particular:

$$\left[\tilde{f}(\mathbf{k})\right]^{\nu} = \tilde{f}(\nu^{1/\beta}\mathbf{k}). \qquad (12.15)$$

Consider now a random walk characterized by the structure function (12.12). Combining Eqs. (12.9) and (12.15) we find the Fourier transform of the PDF for finding the particle at x after ν steps:

$$\bar{n}_\nu(\mathbf{k}) = \exp(-\nu C k^\beta). \tag{12.16}$$

Thus, the PDF keeps at all times the Lévy form; the argument of its characteristic function is simply multiplied by ν, i.e., it is proportional to time. Thus the random walk has in this case an important *self-similarity property*.

The Lévy distribution for the value $\beta = 2$ is simply the Gaussian PDF. In this case the inverse Fourier transform of Eq. (12.16) can be obtained analytically, and is again a Gaussian:

$$n_\nu(\mathbf{x}) = \frac{1}{(4\pi \nu C)^{d/2}} \exp\left(-\frac{r^2}{4\nu C}\right), \quad \beta = 2. \tag{12.17}$$

The corresponding MSD is easily found from Eq. (12.7):

$$\langle r^2 \rangle = 2dC\nu, \quad \beta = 2. \tag{12.18}$$

This MSD thus grows proportionally to time. We thus found the following important property (see Sec. 11.2): *A random walk defined by a Gaussian structure function exhibits* DIFFUSIVE BEHAVIOUR.

Consider now the case when the structure function corresponds to a Lévy distribution with $0 < \beta < 2$. In this case the PDF, i.e., the inverse transform of (12.16), has in general no simple analytic form (except for $\beta = 1$, which corresponds to a Lorentz, or Cauchy distribution, see Appendix). The main qualitative feature of these Lévy distributions is the presence of a *long tail in x*. As a result, *the MSD is infinite for all values of $0 < \beta < 2$*. Indeed, applying Eq. (12.7) to (12.16) we find that $\langle r^2 \rangle \sim k^{\beta-2}\big|_{k=0} = \infty$. For this reason these stable Lévy distributions were for a long time considered as "mathematical monsters" without any physical relevance. It is only recently that the interest of the physicists was revived, as will be seen in forthcoming sections.

We now revert to the general case of an asymmetric PDF, i.e. one for which the first moment differs from zero. We may ask the question: *Why should the stable distributions play a special role in the theory of random walks (or, more generally, in physics)?* Consider a random walk defined by an ARBITRARY STRUCTURE FUNCTION, of which we only require that it be an *analytic function near* $\mathbf{k} = 0$:

$$\bar{f}(\mathbf{k}) = \int d^d x \, e^{i\mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}) = \langle e^{i\mathbf{k}\cdot\mathbf{x}} \rangle, \tag{12.19}$$

where the function $f(\mathbf{x})$ is *not* specified. Expanding the exponential, we obtain:

$$\tilde{f}(\mathbf{k}) = 1 + i\mathbf{k}\cdot\langle\mathbf{x}\rangle - \tfrac{1}{2}\mathbf{k}\mathbf{k} : \langle\mathbf{x}\mathbf{x}\rangle + O(k^3). \tag{12.20}$$

For simplicity, we consider here the case of an *isotropic* transition PDF, for which:

$$\langle x_i x_j\rangle = \delta_{ij}\frac{1}{d}\langle x_n x_n\rangle = \delta_{ij}\frac{1}{d}\langle r^2\rangle\,;$$

(12.20) then reduces to:

$$\tilde{f}(\mathbf{k}) = 1 + i\mathbf{k}\cdot\langle\mathbf{x}\rangle - \frac{1}{2d}k^2\langle r^2\rangle + O(k^3). \tag{12.21}$$

Our assumption of analyticity of $\tilde{f}(\mathbf{k})$ implies that the coefficients of this series, hence the *moments* of $f(\mathbf{x})$, are finite. It is well known, on the other hand, that an arbitrary structure function can be represented, for small k, in terms of *cumulants*, as follows:

$$\tilde{f}(\mathbf{k}) = \exp\left[i\mathbf{k}\cdot\langle\mathbf{x}\rangle - \frac{1}{2d}k^2\langle\langle r^2\rangle\rangle + \ldots\right], \tag{12.22}$$

where the second cumulant is defined as follows:

$$\langle\langle r^2\rangle\rangle = \langle r^2\rangle - |\langle\mathbf{x}\rangle|^2 = \langle|\mathbf{x}-\langle\mathbf{x}\rangle|^2\rangle. \tag{12.23}$$

Hence, *in the limit of small* $\mathbf{k}$, any analytic structure function tends to the form (12.22).

We now introduce the "true" time variable, $t = \nu\tau$, and calculate the density profile which is renamed as $n(\mathbf{x};t) = n_\nu(\mathbf{x})$. Using (12.10) and (12.22) we find:

$$n(\mathbf{x};t) = (2\pi)^{-2d}\int d^d\mathbf{k}\,e^{-i\mathbf{k}\cdot\mathbf{x}}\exp\left[i\,\nu\tau\,\mathbf{k}\cdot\frac{\langle\mathbf{x}\rangle}{\tau} - \frac{1}{2d}k^2\,\nu\tau\,\frac{\langle\langle r^2\rangle\rangle}{\tau} + \ldots\right].$$

Define[2]:

$$\mathbf{V} = \frac{\langle\mathbf{x}\rangle}{\tau}, \quad D = \frac{\langle\langle r^2\rangle\rangle}{2d\,\tau}. \tag{12.24}$$

The second equation is nothing other than the celebrated *Einstein relation*, which we met already in Eq. (9.17). We now find:

$$n(\mathbf{x};t) = (2\pi)^{-2d}\int d^d\mathbf{k}\,e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{V}t)}e^{-k^2 Dt}, \tag{12.25}$$

which yields:

---

[2]Keep in mind that $\langle\mathbf{x}\rangle$ and $\langle\langle r^2\rangle\rangle$ are moments of the transition PDF $f(\mathbf{x})$, not of $n(\mathbf{x};t)$!

$$n(x,t) = \frac{1}{(2\pi\, D\, t)^{d/2}} \exp\left[-\frac{|x - Vt|^2}{4Dt}\right]. \tag{12.26}$$

This function is called a *Gaussian packet*. It represents a density profile which, at time zero, is concentrated at the origin; for $t > 0$ the profile spreads out (*diffusion*) and at the same time its maximum moves at a constant velocity V (*advection*). The shape of the profile at various times is determined by the *Péclet number*, Pe, which measures the relative importance of the advection, compared to the diffusion:

$$Pe = \frac{VL}{D}, \tag{12.27}$$

where L is a characteristic length. In Figs. 12.1.a, 12.1.b, the evolution of the density profile in time (for $d = 1$) is shown for two values of the Péclet number.
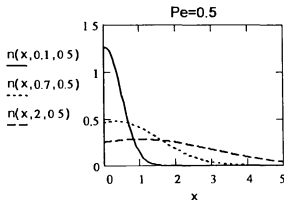

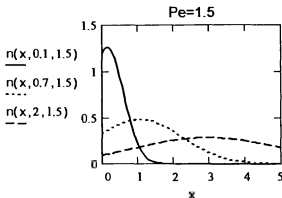Figure 12.1.a. Density profiles at $t = 0.1$, 0.7, 2. Pe $= 0.5$.

Figure 12.1.b. Density profiles at $t = 0.1, 0.7, 2$. Pe = 1.5

Eq. (12.26) was derived in the limit $k \to 0$, which corresponds to $|x - Vt| \to \infty$; thus, for every fixed x, (12.26) represents an asymptotic limit for long times.

The calculation performed above is simply a derivation of the celebrated CENTRAL LIMIT THEOREM of probability theory. It is formulated as follows in the present context: *Any PDF of a random walk having an analytic structure function tends asymptotically to a Gaussian packet.* This is an answer to our question about the special importance of the Gaussian distribution. It should be noted that the Gaussian packet is the Green's function of the *advection-diffusion equation:*

$$\partial_t n(x,t) = D \nabla^2 n(x,t) - V \cdot \nabla n(x,t), \qquad (12.28)$$

i.e., a solution corresponding to the initial condition $n(x,0) = \delta(x)$. For $V = 0$ (i.e., for a symmetric PDF), this equation reduces to the ordinary diffusion equation.

We now made the complete connection with the theory of diffusion based on the Langevin equation or on the hybrid kinetic equation. We found that any *regular* random walk behaves asymptotically as a diffusive process. Its MSD, measured with respect to the maximum of the PDF is:

$$\langle |x - Vt|^2 \rangle = 2d\,D\,t \qquad (12.29)$$

Hence D, as given by (12.24) is identified with the diffusion coefficient (11.9) [3].

The main assumption in the Central Limit Theorem is the analyticity of the structure function. What happens if this condition breaks down? Typically a non-analytic function may have an expansion for small k which contains non-integral powers, such as:

$$\tilde{f}(\mathbf{k}) = 1 - Ck^\beta + ..., \quad 0 < \beta < 2. \tag{12.30}$$

This case is clearly related to the stable Lévy PDF's. It will lead asymptotically to a definitely *non-Gaussian* profile, having an infinite MSD. This PDF does not obey a diffusion equation: we are now in the realm of *strange diffusion*. The theory of these processes will be discussed in the framework of a generalization of the usual random walks in the next sections.

12.2 Continuous Time Random Walks (CTRW)

The idealization of the diffusion process by a random walk in which the jumps take place at regular, well defined times $t = j\tau$ is not very realistic. We now introduce an extremely fruitful generalization of the random walk concept in which time appears as a continuous variable.

In the CONTINUOUS TIME RANDOM WALK (*CTRW*) model, a particle makes a jump $\mathbf{r}$ of arbitrary length and arbitrary direction in a d-dimensional space, then remains at its new position for a finite time T, after which it makes a new jump, etc. It is again assumed that the jumps are statistically independent. *The probability density of a jump described by a vector $\mathbf{r}$ (i.e., the transition PDF) is denoted by $f(\mathbf{r})$* as in the classical problem. But, in contrast to the classical problem, *the jumps are performed at random intervals, that must be defined statistically*. We thus introduce the WAITING TIME DISTRIBUTION $\psi(t)$, defined as *the probability density (PDF) of a pause of duration t between two successive steps*. In other words, $\psi(t)$ represents the PDF that a step is taken at a time t after the previous one. We also introduce the Laplace transform of this function, as well as the corresponding inversion formula:

$$\widehat{\psi}(s) = \int_0^\infty dt \, e^{-st} \, \psi(t), \tag{12.31}$$

$$\psi(t) = \frac{1}{2\pi i} \int_\gamma ds \, e^{st} \, \widehat{\psi}(s), \tag{12.32}$$

---

[3]The presence of the factor $2d$ in Eqs. (12.24), (12.29) is due to our present consideration of the square of the d-dimensional vector $(\mathbf{x} - \mathbf{V}t)$, which is appropriate for an isotropic problem. In Eq. (11.9) we considered diffusion in a single direction x, thus $d = 1$.

where γ is the usual Bromwich contour in the complex s-plane for the inversion of the Laplace transformation, i.e., a parallel to the imaginary axis lying to the right of all singularities of the integrand. [4]

Let now $\psi_j(t)$ represent the PDF that, starting at time $t = 0$, the j-th step is taken at time t. Clearly:

$$
\begin{aligned}
\psi_j(t) &= \int_0^t d\tau\, \psi(t-\tau)\, \psi_{j-1}(\tau), \quad j > 1, \\
\psi_1(t) &= \psi(t).
\end{aligned}
\tag{12.33}
$$

[The interpretation of these relations is obvious from the definitions of the functions $\psi_j(t), \psi(t)$.] In the Laplace representation, the convolution transforms into a product, and we obtain:

$$
\widehat{\psi}_j(s) = \widehat{\psi}(s)\,\widehat{\psi}_{j-1}(s), \quad \widehat{\psi}_1(s) = \widehat{\psi}(s).
\tag{12.34}
$$

This recurrence relation is easily solved:

$$
\widehat{\psi}_j(s) = [\widehat{\psi}(s)]^j \equiv \widehat{\psi}^j(s).
\tag{12.35}
$$

Our main goal will be the calculation of the DENSITY PROFILE $n(x; t)$ defined as the PDF that a particle starting in $x = 0$ at time $t = 0$, be in x at time t. Let $q(x;t)$ be the PDF that the particle arrives in x at time t immediately after a jump; let also $\varphi(t)$ be the PDF that the particle remains immobile during a time t after a jump. Then, clearly:

$$
n(x; t) = \int_0^t d\tau\, \varphi(t-\tau)\, q(x; \tau).
\tag{12.36}
$$

We now calculate the two factors entering the right hand side. We first note that the PDF that at least one step was taken sometime in the interval $(0, t)$ is:

$$
\int_0^t dt'\, \psi(t');
$$

hence, the PDF that the particle remains immobile during the time t after a jump is:

$$
\varphi(t) = 1 - \int_0^t dt'\, \psi(t').
\tag{12.37}
$$

Its Laplace transform is:

---

[4]Here we use the familiar notation s for the (complex) Laplace variable, rather than the notation iz used in Chap. 5. The contour of integration Γ introduced in the latter case [see (5.42)] is replaced here by the more usual form γ of the Bromwich contour.

$$\widehat{\varphi}(s) = \frac{1}{s} - \frac{\widehat{\psi}(s)}{s}. \tag{12.38}$$

In order to calculate $q(\mathbf{x}; t)$ we must take into account all independent ways by which the particle can arrive in x after a jump: it may reach x after one step, two steps, etc. For a j-step process, $q_{(j)}(\mathbf{x}; t)$ is given by the PDF $n_j(\mathbf{x})$ of reaching x after j steps, times the PDF $\psi_j(t)$ that the j-th step was taken at time t [see Eqs. (12.33) - (12.35)]:

$$q(\mathbf{x}; t) = \sum_{j=0}^{\infty} \psi_j(t)\, n_j(\mathbf{x}). \tag{12.39}$$

One easily finds, from the arguments of the previous section, that $n_j(\mathbf{x})$ is related to the transition PDF $f(\mathbf{x})$ in the same way as in the ordinary random walk, Eqn. (12.9). We introduce, for any function $g(\mathbf{x}; t)$ the Fourier transform with respect to x and the Laplace transform with respect to t:

$$\widehat{g}(\mathbf{k}; s) = \int d^d \mathbf{x}\, e^{i\mathbf{k}\cdot\mathbf{x}} \int_0^\infty dt\, e^{-st}\, g(\mathbf{x}; t). \tag{12.40}$$

Transforming in this way Eq. (12.39) and using (12.9) and (12.35) we find:

$$\widehat{q}(\mathbf{k}; s) = \sum_{j=0}^{\infty} \widehat{\psi}_j(s)\, \bar{n}_j(\mathbf{k}) = \sum_{j=0}^{\infty} \widehat{\psi}^j(s)\, \bar{f}^j(\mathbf{k});$$

this geometric series is summed, with the result:

$$\widehat{q}(\mathbf{k}; s) = \frac{1}{1 - \widehat{\psi}(s)\, \bar{f}(\mathbf{k})}. \tag{12.41}$$

We now introduce this result into (12.36), which is Fourier-Laplace (F-L) transformed as follows

$$\widehat{n}(\mathbf{k}; s) = \widehat{\varphi}(s)\, \widehat{q}(\mathbf{k}; s);$$

using Eqs. (12.38) and (12.41) we obtain:

$$\widehat{n}(\mathbf{k}; s) = \frac{1 - \widehat{\psi}(s)}{s} \frac{1}{1 - \widehat{\psi}(s)\, \bar{f}(\mathbf{k})}. \tag{12.42}$$

Transforming back to space and time, we find the density profile:

$$n(\mathbf{x}; t) = (2\pi)^{-d} \int d^d \mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{x}} (2\pi i)^{-1} \int_\gamma ds\, e^{st} \frac{1 - \widehat{\psi}(s)}{s} \frac{1}{1 - \widehat{\psi}(s)\, \bar{f}(\mathbf{k})}. \tag{12.43}$$

Eq. (12.42) or (12.43) is called the MONTROLL-WEISS EQUATION: it yields the complete solution of the Continuous Time Random Walk problem. When the structure function $\tilde{f}(\mathbf{k})$ and the waiting time distribution $\tilde{\psi}(s)$ are given, the density profile is determined by a quadrature. The latter operation is, however, not always expressible in analytic form!

We now show that the density profile $n(\mathbf{x}; t)$ obeys a very interesting integro-differential equation. We recall that the initial condition for this function is: $n(\mathbf{x}; 0) = \delta(\mathbf{x})$, whose Fourier transform is: $\hat{n}(\mathbf{k}; 0) = 1$. Hence, the F-L transform of its time derivative is: $s\,\hat{\overline{n}}(\mathbf{k}; s) - 1$, and we may write, using (12.42):

$$
\begin{aligned}
s\,\hat{\overline{n}}(\mathbf{k}; s) - 1 &= \frac{1 - \tilde{\psi}(s)}{1 - \tilde{\psi}(s)\,\tilde{f}(\mathbf{k})} - 1 \\
&= -\left[1 - \tilde{f}(\mathbf{k})\right]\frac{\tilde{\psi}(s)}{1 - \tilde{\psi}(s)\,\tilde{f}(\mathbf{k})} \\
&= -\left[1 - \tilde{f}(\mathbf{k})\right]\underbrace{\frac{1 - \tilde{\psi}(s)}{s\left[1 - \tilde{\psi}(s)\,\tilde{f}(\mathbf{k})\right]}}_{\hat{\overline{n}}}\frac{s\,\tilde{\psi}(s)}{\left[1 - \tilde{\psi}(s)\right]}
\end{aligned}
$$

We now define the function:

$$
\hat{\phi}(s) = \frac{s\,\tilde{\psi}(s)}{1 - \tilde{\psi}(s)}. \tag{12.44}
$$

We thus obtained:

$$
s\,\hat{\overline{n}}(\mathbf{k}; s) - 1 = -\hat{\phi}(s)\left[1 - \tilde{f}(\mathbf{k})\right]\hat{\overline{n}}(\mathbf{k}; s), \tag{12.45}
$$

or, performing the inverse F-L transformation [and introducing the inverse Laplace transform $\phi(t)$ of $\hat{\phi}(s)$]:

$$
\partial_t n(\mathbf{x}; t) = \int_0^t d\tau\, \phi(t - \tau)\left[-n(\mathbf{x}; t) + \int d^4x'\, f(\mathbf{x} - \mathbf{x}')\, n(\mathbf{x}'; \tau)\right]. \tag{12.46}
$$

This generalized MASTER EQUATION was derived by MONTROLL and SHLESINGER in 1984: it governs the evolution of the density profile in a CTRW. Its most characteristic feature is its *non-Markovian character, both in time and in space*: the rate of change of $n(\mathbf{x}; t)$ is determined by the past history and by the spatial environment. The effective importance of these features is determined by the range of the functions $\phi(t)$ and $f(\mathbf{x})$.

In order to make the connection with the classical random walks, we consider an important special case. Let $\tilde{f}(\mathbf{k})$ be an isotropic structure function of the form given in Eq. (12.21), which we rewrite here for convenience:

$$\tilde{f}(\mathbf{k}) = 1 + i\mathbf{k}\cdot\langle\mathbf{x}\rangle - (2d)^{-1}k^2 \left\langle x^2 \right\rangle. \qquad (12.47)$$

Let also $\hat{\psi}(s)$ be of the form:

$$\boxed{\hat{\psi}(s) = 1 - \langle t\rangle\, s + O(s^2), \quad s \to 0.} \qquad (12.48)$$

Clearly, $\langle t\rangle$ is the first moment of the waiting time distribution, i.e., the average length of the pause between two steps, assumed to be finite. We substitute these expressions into (12.42) and evaluate the latter in the limit $k \to 0, s \to 0$:

$$
\begin{aligned}
\hat{n}(\mathbf{k};s) &\approx \frac{1 - [1 - \langle t\rangle\, s]}{s\,\{1 - [1 - \langle t\rangle\, s]\,[1 + i\mathbf{k}\cdot\langle\mathbf{x}\rangle - (2d)^{-1}k^2 \langle x^2\rangle]\}} \\
&= \frac{\langle t\rangle}{\langle t\rangle\, s - i\mathbf{k}\cdot\langle\mathbf{x}\rangle + (2d)^{-1}k^2 \langle x^2\rangle + [i\mathbf{k}\cdot\langle\mathbf{x}\rangle - (2d)^{-1}k^2 \langle x^2\rangle]\,\langle t\rangle\, s}
\end{aligned}
$$

Neglecting the bracketed terms in the denominator, as being of subdominant order, we find:

$$\hat{n}(\mathbf{k};s) = \frac{1}{s - i\mathbf{k}\cdot\mathbf{V} + Dk^2} \qquad (12.49)$$

with:

$$\mathbf{V} = \frac{\langle\mathbf{x}\rangle}{\langle t\rangle}, \qquad D = \frac{\langle x^2\rangle}{2d\,\langle t\rangle}. \qquad (12.50)$$

The inverse Laplace transform of (12.49) is obtained from the residue of the right hand side at the pole $s = i\mathbf{k}\cdot\mathbf{V} - Dk^2$:

$$\tilde{n}(\mathbf{k};t) = \exp\left(i\mathbf{k}\cdot\mathbf{V}t - Dk^2 t\right). \qquad (12.51)$$

The inverse Fourier transform of this function is precisely the Gaussian packet (12.26). This result proves the generalized *Central Limit Theorem* for the Continuous Time Random Walks:

For any CTRW defined by a transition PDF $f(\mathbf{x})$ having at least finite first and second moments, and a waiting time PDF $\psi(t)$ having at least a first finite moment, the density profile $n(\mathbf{x};t)$ tends to a Gaussian packet for long times and/or large distances.

Although the asymptotic Gaussian packet is the most frequently encountered case in physics, the non-Gaussian processes have attracted much interest in recent years because of their unusual properties and of their relevance in some important physical problems. These are realized whenever the conditions of the Central Limit Theorem

are not satisfied, i.e., when either $f(x)$, or $\psi(t)$, or both, have a *long tail*. We mention briefly the first case, and study the second one in detail in the forthcoming sections.

In the first case we assume that $\hat{\psi}(s)$ has the regular form (12.48), but the structure function is non-analytic:

$$\tilde{f}(\mathbf{k}) = 1 + i\mathbf{k}\cdot\langle\mathbf{x}\rangle - Bk^{\beta} + ..., \quad 0 < \beta < 2, \quad k \to 0, \tag{12.52}$$

[where, as usual, $k = (\mathbf{k}\cdot\mathbf{k})^{1/2}$]. In this case we find an expression for the F-L transform of the density profile similar to (12.49):

$$\hat{\tilde{n}}(\mathbf{k};s) = \frac{1}{s - i\mathbf{k}\cdot\mathbf{V} + bk^{\beta}}, \tag{12.53}$$

where $b = B/\langle t \rangle$. This function represents a *Lévy packet*, i.e., a long-tailed Lévy-like distribution propagating in space with a velocity V.

12.3 The Standard Long-Tail CTRW (SLT-CTRW)

We now define a class of CTRW's that are of particular physical importance. It is defined by a symmetrical and analytic structure function near the origin:

$$\tilde{f}(\mathbf{k}) = 1 - \frac{1}{2d}\sigma^2 k^2 + ..., \quad k \to 0. \tag{12.54}$$

On the other hand, the Laplace transform of the waiting time PDF is non-analytic near $s = 0$

$$\boxed{\hat{\psi}(s) = 1 - \tau_D^{\alpha}s^{\alpha} + ..., \quad 0 < \alpha < 1, \quad s \to 0.} \tag{12.55}$$

A CTRW defined by Eqs. (12.54), (12.55) will be called a STANDARD LONG TAIL CTRW (SLT-CTRW). It is determined by four constant parameters:

- the *dimensionality* of the process: d,

- the *exponent* α,

- the *characteristic length* σ,

- the *characteristic time* τ_D.

[Note that τ_D is *not* to be confused with the average duration of the pauses $\langle t \rangle$ as in (12.47): here $\langle t \rangle = \infty$!]

We now consider the inverse Laplace transform of $\hat{\psi}(s)$: this point must be treated rather carefully. The inverse Laplace transform of the constant 1 is the Dirac delta

function $\delta(t)$. The transformation of s^α requires the application of a so-called Tauberian theorem (see the literature given in BN12). We give here the result:

$$\mathcal{L}_t^{-1}[s^\alpha] = \frac{1}{\Gamma(-\alpha)} t^{-1-\alpha}, \quad s > 0. \quad 0 < \alpha < 1 \ ? \quad (12.56)$$

where we use the following abbreviation for the inverse Laplace transform of a function $g(s)$:

$$\mathcal{L}_t^{-1}[g(s)] = \frac{1}{2\pi i} \int_\gamma ds \, e^{st} g(s). \quad (12.57)$$

$\Gamma(z)$ is the well-known Euler Gamma function. Using also the identity $\Gamma(z+1) = z\Gamma(z)$, we find the waiting time PDF:

$$\psi(t) = \frac{1}{\tau_D} \frac{\alpha}{\Gamma(1-\alpha)} \left(\frac{t}{\tau_D}\right)^{-1-\alpha} + \ldots, \quad t \to \infty. \quad (12.58)$$

The Montroll-Weiss equation (12.42) yields the following asymptotic expression for the Fourier transform of the density profile:

$$\bar{n}(k; t) = \tau_D \mathcal{L}_t^{-1} \left\{ \frac{1}{(\tau_D s)^{1-\alpha} \left[1 - \bar{f}(k)\right] + (\tau_D s)\bar{f}(k)} \right\}. \quad (12.59)$$

Using the following results:

$$\frac{\partial}{\partial k} \cdot \frac{\partial}{\partial k} \bar{f}(k) = -2d\sigma^2,$$

$$\mathcal{L}_t^{-1}(s^{-\gamma}) = \frac{1}{\Gamma(\gamma)} t^{\gamma-1}, \quad \gamma > 0 \quad \text{wie } (12.56) \quad (12.60)$$

we find from Eq. (12.7) the following expression for the mean square displacement (MSD):

$$\langle r^2(t) \rangle = \frac{1}{\Gamma(1+\alpha)} \sigma^2 \left(\frac{t}{\tau_D}\right)^\alpha, \quad 0 < \alpha < 1. \quad (12.61)$$

The SLT-CTRW thus describes a typical case of STRANGE TRANSPORT [5]. This name will denote a transport process for which the MSD behaves asymptotically like a power law, with an exponent different from 1:

---

[5]In the literature this concept is most frequently called "anomalous transport". The latter name is, however, also used for a quite different concept, which will be described in forthcoming chapters. We thus prefer to use a new name for the process described here. The name "strange kinetics" first appeared in a paper by Zaslavsky, Shlesinger and Klafter (BN12).

$$\langle r^2(t) \rangle = Bt^\alpha, \quad t \to \infty. \tag{12.62}$$

The exponent α will be called the DIFFUSION EXPONENT. We thus have the following cases:

$\alpha < 1$	SUBDIFFUSIVE	strange
$\alpha = 1$	DIFFUSIVE	normal
$\alpha > 1$	SUPERDIFFUSIVE	strange
$\alpha = 2$	BALLISTIC	strange

The SLT-CTRW thus describes a typical *subdiffusive* process: it is this feature which makes it particularly interesting for us.

12.4 SLT-CTRW: The Density Profile

We now show that it is possible to derive an asymptotic analytical expression for the density profile $n(x; t)$ of a SLT-CTRW (it only depends on $r = (x \cdot x)^{1/2}$). Starting from the Montroll-Weiss equation (12.42) and using (12.54), (12.55) we find, in the limits $s \to 0$, $k \to 0$ [see the calculation leading to (12.48)]:

$$\tilde{n}(r; s) = \tau_D^\alpha s^{\alpha-1} (2\pi)^{-d} \int d^d x \, e^{-ik \cdot x} \frac{1}{(\tau_D s)^\alpha + \frac{1}{2d}(\sigma k)^2}. \tag{12.63}$$

We do not give here all the detailed algebra involved in the inversion of the F-L integrals of this expression (see BN12). The first important fact that comes out of this calculation is the exact general form of the density profile:

$$\boxed{n(r; t) = \sigma^{-d} \left(\frac{\tau_D}{t} \right)^{\alpha d/2} F(q).} \tag{12.64}$$

The following dimensionless variable is introduced here:

$$q = \left(\frac{\tau_D}{t} \right)^{\alpha/2} \frac{r}{\sigma}. \tag{12.65}$$

$F(q)$ is a (complicated) function depending only on the variable q.

Eq. (12.64) is a typical SCALING RELATION. It tells us, in particular that the density profile depends on r only through the combination q defined in Eq. (12.65). q is called the SIMILARITY VARIABLE. The density profile is thus expressed as a product of three factors:

- The factor σ^{-d} introduces the natural length scale and ensures the correct dimension;

- The second (dimensionless) factor is an explicit function of time alone;

- The third (dimensionless) factor is a function of the similarity variable q alone; its specific form depends on the diffusion exponent α and on the dimensionality d.

Although the function $F(q)$ cannot be calculated analytically in general, its asymptotic behaviour can be obtained in the form:

$$F(q) \sim \exp\left(-bq^{\delta}\right), \qquad \delta = \frac{2}{2-\alpha}, \qquad q \to \infty. \tag{12.66}$$

We thus find a characteristic *stretched exponential* behaviour. We note that in the case $\alpha = 1$, i.e. in the diffusive case, $\delta = 2$ and $F(q)$ reduces to a Gaussian and (12.64) reduces to the Gaussian packet (12.26). We thus recover the prediction of the Central Limit Theorem. This limiting case allows us to fix the value of the constant $b = 1/4$.

Another interesting consequence of the scaling law (12.64) concerns *the moments of the density profile*. These are obtained as follows:

$$\left\langle r^{2p}(t) \right\rangle = \int d^d \mathbf{x}\, r^{2p} \frac{a}{\sigma^d} \left(\frac{\tau_D}{t}\right)^{\alpha d/2} F(q).$$

We make the change of integration variable $\mathbf{x} \to \sigma\, (t/\tau_D)^{\alpha/2}\, \mathbf{y}$ [note that $\mathbf{y} \cdot \mathbf{y} = q^2$]:

$$\left\langle r^{2p}(t) \right\rangle = \sigma^{d+2p} \left(\frac{t}{\tau_D}\right)^{(d+2p)\alpha/2} \sigma^{-d} \left(\frac{t}{\tau_D}\right)^{-\alpha d/2} a \int d^d \mathbf{y}\, y^{2p} F(y)$$

Noting that the last integral over q is a mere constant, we find:

$$\left\langle r^{2p}(t) \right\rangle = \sigma^{2p} M_p \left(\frac{t}{\tau_D}\right)^{p\alpha}. \tag{12.67}$$

We thus obtained a SCALING LAW for the moments. We note that the scaling exponent $p\alpha$ is independent of the dimensionality d of the space. Moreover, the form of the function $F(q)$ does not influence the value of this exponent: it merely determines the value of the constant M_p. The value of the latter depends on the order p, on the diffusion exponent α and on the dimensionality d. The two parameters defining the SLT-CTRW, i.e. σ and τ_D, appear in (12.67) as natural units of length and time, respectively. For $p = 1$, Eq. (12.67) reduces, of course to (12.61). In this particular case the constant M_p is independent of d. The present calculation cannot yield the value of the coefficient M_p; the latter will be obtained explicitly, however, in the next section.

We now specialize these results to the *one-dimensional SLT-CTRW* ($d = 1$), which is of interest in many applications. It can first be shown that the Laplace transform of the density profile has the following form in this case:

$$\tilde{n}(x; s) = \frac{1}{\sqrt{2}} \frac{\tau_D}{\sigma} (\tau_D s)^{(\alpha - 2)/2} e^{-q}, \quad d = 1, \quad (12.68)$$

where:

$$q = \sqrt{2} (\tau_D s)^{\alpha/2} \frac{x}{\sigma}, \quad d = 1. \quad (12.69)$$

The inverse Laplace transformation can be done asymptotically (by a steepest descent method) and leads to the form:

$$n(x; t) = \frac{1}{\sigma} \frac{\delta}{2^{3-\alpha} \Gamma\left(\frac{4-\alpha}{2}\right)} \left(\frac{t}{\tau_D}\right)^{-\alpha/2} \exp\left(-\frac{q^{2/(2-\alpha)}}{4}\right), \quad q \gg 1, \quad d = 1. \quad (12.70)$$

This function represents a *long-tailed density profile*. It is plotted in the next section, where it is compared to a related Gaussian packet.

12.5 SLT-CTRW: The Non-Markovian Diffusion Equation

In Sec. 12.2 the Montroll-Shlesinger Equation (12.46) was derived for a general CTRW. Our purpose here is to derive its specific form for the SLT-CTRW and to study some of its properties.

We consider the SLT-CTRW defined by Eqs. (12.54) and (12.55). Its asymptotic F-L density profile was obtained from the Montroll-Weiss equation (12.42) in the limit $\tau_D s \ll 1, \sigma k \ll 1$ [see (12.63)]:

$$\widehat{\tilde{n}}(k; s) = \tau_D \frac{(\tau_D s)^{\alpha - 1}}{(\tau_D s)^\alpha + \frac{1}{2\mu}(\sigma k)^2}. \quad (12.71)$$

It is easily checked that this function satisfies the master equation (12.45) with the kernel $\widehat{\phi}(s)$ defined by (12.44), which reduces to:

$$\widehat{\phi}(s) = \frac{1}{\tau_D} \frac{1 - (\tau_D s)^\alpha}{(\tau_D s)^{\alpha - 1}},$$

which is simplified by retaining only the leading term for $\tau_D s \ll 1$:

$$\widehat{\phi}(s) = \frac{1}{\tau_D} (\tau_D s)^{1-\alpha}. \quad (12.72)$$

The F-L master equation (12.45) becomes:

$$s\,\hat{n}(k;s) - 1 = -\hat{\phi}(s)\,\frac{1}{2d}\,(\sigma k)^2\,\hat{n}(k;s). \tag{12.73}$$

The inverse Fourier transform of this equation is [we recall that the initial value of the density profile is: $n(x;t=0) = \delta(x)$]:

$$s\hat{n}(x;s) - \delta(x) = \frac{\sigma^2}{2d}\,\hat{\phi}(s)\,\nabla^2\hat{n}(x;s). \tag{12.74}$$

This looks very much like a Laplace-transformed diffusion equation; the diffusion coefficient in Laplace space is, however, s-dependent. As a result, the inverse Laplace transform of (12.74) is an integral equation:

$$\boxed{\partial_t n(x;t) = \int_0^t d\tau\, H(\tau)\,\nabla^2 n(x; t - \tau),} \tag{12.75}$$

with:

$$\boxed{H(t) = \frac{\sigma^2}{2d}\,\phi(t).} \tag{12.76}$$

Our main conclusion at this point is: *The density profile of a Standard Long-Tail CTRW obeys a linear, non-Markovian equation*. Given the obvious resemblance of this equation with the diffusion equation, we call it the NON-MARKOVIAN DIFFUSION EQUATION. Note that, in contrast to the general case (12.46) this equation is Markovian with respect to the spatial variable: this is because of the analytic form of the structure function $f(k)$: the term $-k^2$ yields the Laplace operator in physical space. On the other hand, the rate of change of the density profile is influenced by its past history. Given the *long tail* of the memory kernel $H(t)$, the range of effective influence extends far into the past. It is this feature that is responsible for the non-Gaussian character of the density profile and the strange transport law.

In order to calculate the kernel $H(t)$ we note that $\hat{\phi}(s)$ can be simply related to the Laplace transform of the waiting time distribution, $\hat{\psi}(s)$ defined in (12.55):

$$\boxed{\hat{\phi}(s) = \frac{1}{\tau_D}\,(\tau_D s)^{1-\alpha} = \frac{1}{\tau_D}\left[1 - \hat{\psi}_{1-\alpha}(s)\right],}$$

where $\hat{\psi}_{1-\alpha}(s)$ denotes the function $\hat{\psi}(s)$ in which the index α is changed to $1-\alpha$. We evaluate the inverse Laplace transform as explained in Sec. 12.3: the transform of 1 is $\delta(t)$, which can be written for convenience as $\tau_D\,\delta(t/\tau_D)$; the transform of the second term is given *asymptotically* by the Tauberian theorem (12.60) [we note, indeed, that $1-\alpha > 0$ for $0 < \alpha < 1$]:

$$H(t) = \frac{\sigma^2}{2d\tau_D}\left[\delta\left(\frac{t}{\tau_D}\right) - \frac{1-\alpha}{\Gamma(\alpha)}\left(\frac{\tau_D}{t}\right)^2{}^\alpha\right]. \tag{12.77}$$

The delta-function is zero for $t > 0$; we keep it here, however, because it will help us in the derivation of a useful form of the equation of evolution. Substituting this form into (12.75) we find:

$$\partial_t n(\mathbf{x}; t) = D_0 \nabla^2 n(\mathbf{x}; t) - H_0 \int_0^t d\tau \left(\frac{\tau_D}{\tau}\right)^{2-\alpha} \nabla^2 n(\mathbf{x}; t - \tau), \qquad (12.78)$$

where:

$$D_0 = \frac{\sigma^2}{2d\tau_D}, \qquad H_0 = \frac{1 - \alpha}{\Gamma(\alpha)} \frac{1}{\tau_D} D_0. \qquad (12.79)$$

Eq. (12.78) describes the evolution as a superposition of an ordinary diffusion term, with a diffusion coefficient D_0, and a **non-Markovian** process represented by the second term. We recall that we already encountered a non-Markovian diffusion equation in Chap. 11, see Eq. (11.49). In that case, however, a Markovian approximation was fully justified by the exponential decay of the autocorrelation function (see Sec. 12.6). The characteristic feature of the kernel in (12.78) is its *long tail* (see also the remarks at the end of Sec. 11.5): it decreases very slowly, as an inverse power law (note that $2 - \alpha > 0$). A very interesting feature appears in the definition of the coefficient H_0: this coefficient vanishes for $\alpha = 1$. Thus, *in the diffusive case, $\alpha = 1$, the non-Markovian term in (12.78) disappears, and we are left with a pure diffusion equation.*

As it stands, however, Eq. (12.78) does not really make sense; indeed, the kernel $\tau^{-2+\alpha}$ diverges at the lower limit $\tau = 0$. This is not surprising, because the expression of $H(t)$ obtained in (12.77) is an *asymptotic* expression, valid for long times, and certainly inapplicable for $t \to 0$. In order to cure this difficulty, we introduce a *lower cut-off* $\tau_{\min}$ in the integral of Eq. (12.78), which will be determined below. The equation of evolution is thus written in the following, final form:

$$\partial_t n(\mathbf{x}; t) = D_0 \nabla^2 n(\mathbf{x}; t) - H_0 \int_{\tau_{\min}}^t d\tau \left(\frac{\tau_D}{\tau}\right)^{2-\alpha} \nabla^2 n(\mathbf{x}; t - \tau). \qquad (12.80)$$

In order to define a criterion for the determination of the cut-off, we consider the moments of this equation, beginning with the second moment, i.e., the MSD. This moment was determined independently in Eq. (12.61) and was shown to scale asymptotically as $\langle r^2(t) \rangle \sim t^\alpha$, thus: $\partial_t \langle r^2(t) \rangle \sim t^{\alpha-1}$. We now calculate its rate of change by using Eq. (12.80):

$$\partial_t \langle r^2(t) \rangle = \int d^d x \, r^2 \left\{ D_0 \nabla^2 n(\mathbf{x}; t) - H_0 \int_{\tau_{\min}}^t d\tau \left(\frac{\tau_D}{\tau}\right)^{2-\alpha} \nabla^2 n(\mathbf{x}; t - \tau) \right\}.$$

We perform an integration by parts over $\mathbf{x}$ and note that:

$$\int d^d x \, r^2 \, \nabla^2 n(\mathbf{x};t) = 2d, \quad \forall t.$$

We thus obtain, using (12.79):

$$\partial_t \left\langle r^2(t) \right\rangle = 2dD_0 \left\{ 1 - \frac{1-\alpha}{\Gamma(\alpha)\,\tau_D} \int_{\tau_{\min}}^t d\tau \left(\frac{\tau_D}{\tau} \right)^{2-\alpha} \right\}$$

$$= 2dD_0 \left\{ 1 + \frac{1}{\Gamma(\alpha)} \frac{t^{\alpha-1} - \tau_{\min}^{\alpha-1}}{\tau_D^{\alpha-1}} \right\}.$$

This expression contains a term which has the correct scaling, $\sim t^{\alpha-1}$, and a term that is constant, which would dominate for $\alpha < 1$ and $t \to \infty$. The latter term is thus spurious. But, we can use our freedom for defining the cut-off $\tau_{\min}$ in such a way as to annull this term; this leads to the value:

$$\tau_{\min} = [\Gamma(\alpha)]^{-1/(1-\alpha)} \, \tau_D. \tag{12.81}$$

With this choice of the cut-off, we obtain:

$$\partial_t \left\langle r^2(t) \right\rangle = 2dD_0 \frac{1}{\Gamma(\alpha)} \left(\frac{t}{\tau_D} \right)^{\alpha-1},$$

and consequently, using (12.79):

$$\partial_t \left\langle r^2(t) \right\rangle = 2dD_0\tau_D \frac{1}{\alpha\Gamma(\alpha)} \left(\frac{t}{\tau_D} \right)^{\alpha} = \frac{\sigma^2}{\Gamma(1+\alpha)} \left(\frac{t}{\tau_D} \right)^{\alpha}.$$

This is precisely identical to Eq. (12.61). This result shows that the diffusion term in (12.80) is, in a sense, spurious: it compensates the error originating from the inaccurate short-time domain: the really physical mechanism of evolution is in the long-tail non-Markovian operator.

The validity of Eq. (12.80) is, however, not yet completely settled. Although it yields the correct second moment of the density profile, we should also worry about the higher order moments! In order to determine the latter, we first note the following identity:

$$\nabla^2 r^{2p} = 2p \, (2p + d - 2) \, r^{2p-2}. \tag{12.82}$$

We then derive from (12.80) the following recursion relation for the moments:

$$\partial_t \left\langle r^{2p}(t) \right\rangle = 2p \left(2p + d - 2 \right) D_0$$
$$\times \left\{ \left\langle r^{2p-2}(t) \right\rangle - \frac{1-\alpha}{\Gamma(\alpha)\,\tau_D} \int_{\tau_{\min}}^{t} d\tau \left(\frac{\tau_D}{\tau} \right)^{2-\alpha} \left\langle r^{2p-2}(t-\tau) \right\rangle \right\}$$
(12.83)

The general scaling of the moments was derived in (12.67):

$$\left\langle r^{2p}(t) \right\rangle = C_p t^{p\alpha},$$
(12.84)

which, upon substitution into (12.83) yields:

$$p C_p t^{p\alpha-1} = 2p \left(2p + d - 2 \right) D_0$$
$$\times \left\{ C_{p-1} t^{(p-1)\alpha} - \frac{1-\alpha}{\Gamma(\alpha)} \tau_D^{1-\alpha} C_{p-1} \int_{\tau_{\min}}^{t} d\tau \, \tau^{\alpha-2} (t-\tau)^{(p-1)\alpha} \right\}.$$
(12.85)

The value of the integral can be obtain (e.g., by the MATHEMATICA program):

$$\int_{\tau_{\min}}^{t} d\tau \, \tau^{\alpha-2} (t-\tau)^{(p-1)\alpha} = \frac{\Gamma(\alpha-1)\,\Gamma\left[1 + \alpha(p-1)\right]}{\Gamma\left[\alpha + \alpha(p-1)\right]} t^{p\alpha-1}$$
$$+ \frac{\tau_{\min}}{1-\alpha} t^{\alpha(p-1)} {}_2F_1 \left[-1 + \alpha, -\alpha(p-1), \alpha, (\tau_{\min}/t) \right],$$

where ${}_2F_1 [...]$ is a hypergeometric function which, for small values of its last argument, behaves like $1 + O(\tau_{\min}/t)$. Thus, asymptotically, Eq. (12.85) yields:

$$p C_p t^{p\alpha-1} = 2p \left(2p + d - 2 \right) D_0 C_{p-1}$$
$$\times \left\{ t^{(p-1)\alpha} - (1-\alpha) \tau_D^{\alpha-1} \frac{\Gamma(\alpha-1)\Gamma\left[1 + \alpha(p-1)\right]}{\Gamma(\alpha)\Gamma(p\alpha)} t^{p\alpha-1} - \left(\frac{\tau_{\min}}{\tau_D} \right)^{\alpha-1} \frac{1}{\Gamma(\alpha)} t^{(p-1)\alpha} \right\}.$$
(12.86)

We see again in the right hand side two terms proportional to $t^{(p-1)\alpha}$ which do not have the same scaling as the left hand side. Their coefficient must therefore be put to zero, thus:

$$1 - \left(\frac{\tau_{\min}}{\tau_D} \right)^{\alpha-1} \frac{1}{\Gamma(\alpha)} = 0.$$

This yields the *same* value for τ_{min} as Eq. (12.81). This result is very important; it guarantees that *the non-Markovian diffusion equation (12.80), combined with the definition (12.81) for the cut-off, yields the correct values for all the moments of the density profile, hence for the profile itself.*

It is now easily seen that, using some identities for the Γ-functions, (12.86) reduces to:

$$C_p = 2(p-1)(2p+d-1)\frac{\Gamma[\alpha(p-1)]}{\Gamma(\alpha p)}D_0\tau_D^{1-\alpha}C_{p-1}.$$

This recurrence relation is easily solved:

$$C_p = \frac{2^p(p-1)!\,d(d+2)...(d+2p-2)}{\alpha\Gamma(p\alpha)}\left(D_0\tau_D\right)^p\tau_D^{-\alpha}.$$

This form is substituted into (12.84), thus obtaining the general form of the 2p-th moment. It is more convenient to use the definition (12.79) to write the moment in the form (12.67):

$$\left\langle r^{2p}(t)\right\rangle = \sigma^{2p}M_p\left(\frac{t}{\tau_D}\right)^{p\alpha}, \tag{12.87}$$

with the following explicit value for the coefficient:

$$M_p = \frac{d(d+2)...(d+2p-2)}{d^p}\frac{(p-1)!}{\alpha\,\Gamma(p\alpha)}. \tag{12.88}$$

This coefficient gives the final solution for all the moments of the SLT-CTRW, for arbitrary diffusion exponent α ($0 < \alpha \leq 1$), arbitrary order p and arbitrary dimensionality d. It is hardly necessary to emphasize that all the moments are independent of the cut-off τ_{min}.

It is interesting to discuss some special cases. Consider first the MSD, i.e., the case $p = 1$, in arbitrary dimensionality. Recalling that $\alpha\Gamma(\alpha) = \Gamma(\alpha + 1)$, we see that (12.88) reduces to:

$$M_1 = \frac{1}{\Gamma(\alpha+1)}, \quad p = 1, \quad \forall d. \tag{12.89}$$

This result agrees with (12.61). Thus, the MSD is the only moment whose value is independent of the dimensionality d.

Next, we consider the *diffusive case*, $\alpha = 1$, for arbitrary dimensionality. In this case we have $\alpha\Gamma(p\alpha) = \Gamma(p) = (p-1)!$ and Eq. (12.88) reduces to:

$$M_p = \frac{d(d+2)...(d+2p-2)}{d^p}, \quad \alpha = 1, \quad \forall p. \tag{12.90}$$

This is a quite interesting case. In order to derive the moments in the diffusive case, one may start from Eq. (12.78) in which the non-Markovian term is deleted, because $H_0 \sim (1 - \alpha)$. We are then left with an ordinary diffusion equation, from which we derive a recursion equation which is simply (12.83) without the non-Markovian term:

$$\partial_t \left\langle r^{2p}(t) \right\rangle = 2p(2p + d - 2) D_0 \left\langle r^{2p-2}(t) \right\rangle \tag{12.91}$$

For $p = 1$, this reduces to $\partial_t \left\langle r^2(t) \right\rangle = 2dD_0$, with the well-known diffusive form for the MSD: $\left\langle r^2(t) \right\rangle = 2dD_0 t$. From this starting point, the recursion equation (12.91) is solved by successive iteration, yielding the same solution as (12.90). The surprising feature is that in the derivation of (12.88), at the step (12.86), the contribution of the diffusive term, i.e., the first term in the right hand side of (12.86), is exactly cancelled by the third term. Hence, the expression (12.88), valid for arbitrary $\alpha < 1$, results entirely from the non-Markovian term in the equation of evolution. Nevertheless, when extrapolated to $\alpha = 1$, the result connects smoothly to the result obtained from the "pure" diffusion equation.

Another special case that will be of interest in applications is the one-dimensional case ($d = 1$) for arbitrary α. In this case we note:

$$\frac{d(d+2)...(d+2p-2)(p-1)!}{d^p} = 1 \cdot 3 \cdot 5...(2p-1) \cdot 1 \cdot 2 \cdot 3...(p-1)$$

$$= 1 \cdot 3 \cdot 5...(2p-1) \cdot \frac{2 \cdot 4...(2p-2)}{2^{p-1}} = \frac{(2p-1)!}{2^{p-1}}.$$

Thus:

$$M_p = \frac{(2p-1)!}{2^{p-1}} \frac{1}{\alpha \Gamma(p\alpha)}, \quad d = 1, \quad \forall \alpha, \forall p. \tag{12.92}$$

12.6 Markovian vs. Non-Markovian Evolution

We now illustrate more concretely some consequences of the results obtained in this chapter. In order to be specific, we choose the following values for the diffusion exponent and for the dimensionality in a SLT-CTRW process:

$$\alpha = \tfrac{1}{2}, \quad d = 1. \tag{12.93}$$

This case is of interest in several physical applications (for instance: dispersion of charged particles in a turbulent magnetic field). The general asymptotic solution of the SLT-CTRW was derived in Sec. 12.4; in one dimension this was given in Eq. (12.70) which, for $\alpha = \tfrac{1}{2}$ reduces to:

$$n_{SLT}(x;t) = \frac{1}{\sigma}\frac{1}{2^{5/2}\,\Gamma(\frac{7}{4})}\left(\frac{\tau_D}{t}\right)^{1/4}\exp\left(-\frac{q^{4/3}}{4}\right). \tag{12.}$$

One recognizes the general form of the *scaling law* (12.64). The similarity varia, q, defined in (12.65) is here:

$$q = \left(\frac{\tau_D}{t}\right)^{1/4}\frac{x}{\sigma}. \tag{12.}$$

This function is plotted in Fig. 12.2 as a function of the similarity variable at th. different times (solid: $t = 1$, dash-dot: $t = 10$, dash: $t = 100$).
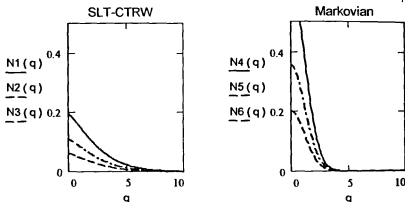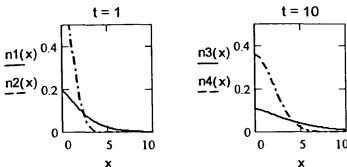

Figure 12.2. Density profiles vs. similarity variable.

In Fig. 12.3 it is shown (solid line) as a function of distance x at two differen times It should be recalled that the initial condition is $n(x;t = 0) = \delta(x)$.

Figure 12.3. Density profiles vs. x at two times.

We know that the SLT profile can also be characterized as the propagator of the non-Markovian diffusion equation (12.80), with the cut-off (12.81); this equation reduces in the present case to:

$$\partial_t n_{SLT}(x;t) = D_0 \nabla_x^2 n_{SLT}(x;t) - H_0 \int_{n-1}^{t} d\tau \left(\frac{\tau_D}{\tau}\right)^{3/2} \nabla_x^2 n_{SLT}(x;t-\tau), \quad (12.96)$$

with:

$$D_0 = \frac{\sigma^2}{2\tau_D}, \qquad H_0 = \frac{1}{2\sqrt{\pi\tau_D}} D_0. \qquad (12.97)$$

We note the slowly decaying, long-tailed memory kernel which decreases like $\tau^{-3/2}$. Non-Markovian equations appeared already in several places in this book. In kinetic theory we derived the Prigogine-Résibois Master Equation (6.4); in the theory of transport equations we encountered a non-Markovian equation relating fluxes to thermodynamic forces (10.56); in the theory of the hybrid kinetic equation we found Eq. (11.49) which is very similar to (12.80). In all these cases, we used a *Markovian approximation* for the simplification of the equations. The argument was based on the existence of two separate time scales: the memory kernel was supposed to decay in a time which is very short compared to the characteristic time of variation of the unknown function. In this case the retardation in the latter can be neglected, and the equation is Markovianized.

We may try to apply this procedure to Eq. (12.80) (without asking questions about its validity at this point!) we consider here the general case (arbitrary values for $0 < \alpha < 1$ and d). We replace $n(x; t - \tau)$ under the integral, and denote by $n_M(x; t)$ the solution of the resulting Markovianized equation:

$$\partial_t n_M(x; t) = D_0 [1 - A(t)] \nabla^2 n_M(x; t),$$

where:

$$1 - A(t) = 1 - \frac{1 - \alpha}{\tau_D \Gamma(\alpha)} \int_{\tau_{\min}}^{t} d\tau \left(\frac{\tau_D}{\tau} \right)^{2 - \alpha}$$

$$= 1 - \frac{1}{\Gamma(\alpha)} \left(\frac{\tau_D}{\tau_{\min}} \right)^{1 - \alpha} + \frac{1}{\Gamma(\alpha)} \left(\frac{\tau_D}{t} \right)^{1 - \alpha}.$$

Note that we did not take the extreme step of letting the upper limit of the integral go to infinity! The two first terms on the right hand side cancel each other exactly for the value (12.81) of the cut-off, and we are left with:

$$\partial_t n_M(x; t) = \frac{D_0}{\Gamma(\alpha)} \left(\frac{\tau_D}{t} \right)^{1 - \alpha} \nabla^2 n_M(x; t). \tag{12.98}$$

Thus, the Markovianized equation of evolution is a diffusion equation with a time-dependent diffusion coefficient. Note that this coefficient tends to zero like $t^{-1 + \alpha}$: Eq. (12.98) describes, indeed, a *subdiffusive* process, as we already know. It is for this reason that the "complete" Markovianization (i.e., letting $t \to \infty$ in the integral) would lead to a trivial result here. This can also be seen in the calculation of $1 - A(t)$ which yields zero for $t = \infty$. The complete Markovianization is only applicable for a diffusive process.

Eq. (12.98) can be solved analytically. The change of variable $t \to T = t^\alpha$, $\nu(x; T) = n_M(x; T^{1/\alpha})$ transforms it into a diffusion equation with a constant coefficient:

$$\partial_T \nu(x; T) = \mathcal{D} \nabla^2 \nu(x; T),$$

with:

$$\mathcal{D} = \frac{D_0}{\Gamma(\alpha + 1)} \tau_D^{1 - \alpha}.$$

The propagator of this equation is given in Eq. (12.26) [for V = 0]; in the resulting equation we revert to the original time variable and find:

$$n_M(x; t) = \sigma^{-d} \left[\frac{d\, \Gamma(\alpha + 1)}{\pi} \right]^{d/2} \left(\frac{\tau_D}{t} \right)^{\alpha d/2} \exp \left[-\frac{d\, \Gamma(\alpha + 1)}{2} q^2 \right]. \tag{12.99}$$

This function has the correct scaling form (12.64), with the similarity variable q defined by (12.65). The scaling function $F(q)$ is, however, quite different from (12.66): *the Markovianized propagator is a Gaussian profile* instead of the stretched exponential $\exp(-bq^\delta)$ *with* $\delta = 2/(2 - \alpha)$. Note, however, that the MSD of this process goes like t^α, which is in agreement with the subdiffusive character. Moreover, Eq. (12.99) cannot be obtained from the correct solution of the non-Markovian equation by any limiting solution. In the specific case studied above, (12.93) the Markovian density profile reduces to:

$$n_M(\mathbf{x}; t) = \sigma^{-1} \frac{1}{(2\sqrt{\pi})^{1/2}} \left(\frac{\tau_D}{t}\right)^{1/4} \exp\left(-\frac{\sqrt{\pi}}{4} q^2\right), \quad \alpha = \frac{1}{2}, d = 1 \quad (12.100)$$

This function is shown in Fig. 12.2 and in Fig. 12.3 (dash-dotted line) together with the exact solution. A comparison of the two curves shows very clearly the long tail of the SLT-CTRW density profile, which is definitely lost in the Markovian "approximation".

The main conclusion of this Section is that *the Markovian approximation is completely inadequate in the SLT-CTRW.* The deep reason thereof is the long tail of the waiting time distribution. Indeed, the resulting memory kernel has a power law dependence on time. Such a function has *no characteristic length*. We cannot therefore define two separate time scales as in the previously treated non-Markovian equations. It is precisely in this feature that the STRANGE TRANSPORT differs fundamentally from the normal one.

We may also look at this question as follows. Consider a *diffusive CTRW* defined by Eqs. (12.47), (12.48). It obeys, in F-L representation, the equation of evolution (12.45), with the memory kernel:

$$\widehat{\varphi}(s) = \frac{s\widehat{\psi}(s)}{1 - \widehat{\psi}(s)} = \frac{1}{\langle t \rangle} - s = \frac{1}{\langle t \rangle}[1 + O(s)]. \quad (12.101)$$

The leading term, for $s \to 0$, is thus the constant $\langle t \rangle^{-1}$. Substituting this into (12.45) we find:

$$s\widehat{n}(k; s) - 1 = -\frac{\langle r^2 \rangle}{2d\,\langle t \rangle} k^2 \,\widehat{n}(k; s),$$

which is precisely the F-L transform of the correct diffusion equation:

$$\partial_t n(r; t) = D \nabla^2 n(r; t), \quad (12.102)$$

Comparing (12.101) with the memory kernel (12.72) of the SLT-CTRW we see that the latter behaves like $s^{1-\alpha}$, which goes to zero for $s \to 0$. Thus, the leading term is

necessarily s-dependent, which implies a non-Markovian equation of evolution. This argument clearly shows that *the Markovian approximation is valid only for diffusive processes.*

12.7   Appendix. Stable Probability Distribution Functions

We introduce the subject by formulating the following problem: *Let $n(x)$ be the PDF of a random d-dimensional random variable x. What is the PDF $n_a(x)$ of the random variable $v = a^{-1}x$, where $a > 0$ is an arbitrary positive constant?*

As v is linearly related to x, we have: $n_a(x) = C_a n(a^{-1}x)$. The constant C_a is determined by expressing that both PDF's are normalized to one. One thus finds the relation:

$$n_a(x) = a^{-d} n(a^{-1}x).\tag{12.103}$$

The corresponding transformation law for the characteristic function (12.2) is easily obtained by a change of integration variable in the Fourier integral:

$$\bar{n}_a(k) = \bar{n}(ak).\tag{12.104}$$

For simplicity, we consider here symmetric PDF's, depending only on $r = (x \cdot x)^{1/2}$; their characteristic functions depend on the absolute value k of the vector k. We now ask for the most general form of a STABLE LAW, defined by the following *form-invariance property*:

$$\bar{n}(a_1k)\,\bar{n}(a_2k) = \bar{n}(ak),\tag{12.105}$$

where a is a positive constant, depending on a_1, a_2. It is easily checked that the solution must be of the form $\bar{n}(k) = \exp\left[-C\,k^{\beta}\right]$, with:

$$a = \left(a_1^{\beta} + a_2^{\beta}\right)^{1/\beta}$$

The possible values of the constants must, however, be limited. For convergence, C must be positive; for regularity in $k = 0$, β must also be positive. Moreover, it can be shown that when $\beta > 2$, the inverse Fourier transform, i.e., the PDF, is not definite positive, hence is not acceptable. In conclusion:

A stable law is characterized by a characteristic function of the form:

$$\bar{n}_{\beta}(k) = \exp\left[\;Ck^{\beta}\right],\quad C > 0,\quad 0 < \beta \le 2.\tag{12.106}$$

The corresponding distribution function is:

$$n_\beta(\mathbf{x}) = (2\pi)^{-d} \int d^d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{x}}\, e^{-C k^\beta}. \tag{12.107}$$

Any PDF of this form is called a LÉVY DISTRIBUTION FUNCTION. These functions were first considered, for general β by Cauchy in 1853; he was, however, not aware that, for $\beta > 2$, they may become negative for some values of $\mathbf{x}$.

The best known stable function is the one corresponding to $\beta = 2$: it is simply the Gaussian, (12.26) with $V = 0$. Its importance stems from the central limit theorem discussed in Sec. 12.1. Another important and simple case is $\beta = 1$: the corresponding stable distribution is called the *Cauchy (or Lorentz) distribution*:

$$n_1(r) = \frac{1}{\pi}\,\frac{1}{1+r^2}. \tag{12.108}$$

Apart from two other cases which can be reduced to special functions ($\beta = \frac{1}{2}$ is related to Fresnel integrals, $\beta = \frac{2}{3}$ is related to the Whittaker function), the Lévy distributions cannot be expressed in close analytic form. One can, however, determine exactly their value for $r = 0$:

$$n_\beta(0) = \frac{1}{\pi\beta}\,\Gamma\left(\frac{1}{\beta}\right). \tag{12.109}$$

This function varies very little around 0.3 for $\beta > 0.5$, but grows very rapidly towards infinity for $\beta < 0.5$. This implies that the shape of the Lévy functions is rather smooth and not too different from a Gaussian in the first case, but becomes suddenly very sharply peaked, rather δ-like, for $\beta < 0.5$. In all cases, the main feature of the Lévy functions is their *long tail*. As a result, all these PDF's, except the Gaussian, have an *infinite second moment*. This is readily checked by applying Eq. (12.7) to (12.106). An interesting representation due to Montroll and Bendler is:

$$n_\beta(r) = \frac{\Gamma(1/\beta)}{\pi\beta}\exp\left(-\frac{r^2}{2\sigma_\beta^2}\right) + \frac{\beta}{2r^{\beta+1}}\exp\left(-\frac{1}{r^\beta}\right), \tag{12.110}$$

with:

$$\sigma_\beta = \left(\frac{\pi}{2}\right)^{1/2}\frac{(1-e^{-1})\beta}{\Gamma(1/\beta)}. \tag{12.111}$$

This representation is particularly useful for small β. The first term represents a very narrow Gaussian, which approximates the δ-like peak and yields the correct value in $r = 0$, whereas the second term (which vanishes at the origin) describes the long tail. Many other useful properties and representations of the Lévy distributions are given in the review paper of Montroll and Bendler (BN12).

12.8   Bibliographical Notes BN12

The references on stochastic properties quoted in BN9 all contain a discussion of classical random walks.

The *stable distributions* were discussed in a general framework in:

Lévy, P., 1937, *Théorie de l'addition des variables aléatoires*, Gauthier-Villars, Paris.

More recent references are:

Wintner, A., 1941, Duke Math. J., **8**, 678,
Montroll E.W. and Bendler, J.T., 1984, J. Stat. Phys., **34**, 129,
Bouchaud, J.P. and Georges, A., 1990, Phys. Rep., **195**, 127.

An attempt toward the incorporation of Lévy distributions into statistical mechanics is found in:

Tsallis, C., Levy, S., Souza, A. and Maynard, R., 1995, Phys. Rev. Lett., **75**, 3589.

The *Continuous Time Random Walks* were introduced by:

Montroll, E.W. and Weiss, G.H., 1965, J. Math. Phys., **6**, 167.

Remarkably clear expositions of their theory is given in the following references:

Montroll, E.W. and Shlesinger, M.F., 1984, in: *Studies of Statistical Mechanics*, vol. **11**, p. 5 (J.L. Lebowitz and E.W. Montroll, eds.), North Holland, Amsterdam [This review paper also contains a delightful history of probability theory],

Weiss, G.H., 1994, *Aspects and Applications of Random Walks*, North Holland, Amsterdam;

Shlesinger, M., 1996, in: *Encyclopaedia of Applied Physics*, vol. **16**, p. 45 [This article contains un updated historical section].   see also:

Bouchaud and Georges (quoted above),
Shlesinger, M.F., Zaslavsky, G.M. and Klafter, J., 1993, Nature, **363**, 31,
Klafter, J., Shlesinger, M.F. and Zumofen, G., 1996, Phys. Today, February, p. 33.

The most complete exposition of the *Tauberian theorems* is found in:

Doetsch, G., 1955, *Handbuch der Laplace Transformation*, (2 volumes), Birkhäuser, Basel.

see also: Weiss, G.H., 1994 (quoted above).

The calculations relative to Sec. 12.4 can be found in:

Ball, R.C., Havlin, S. and Weiss, G.H., 1987, J. Phys., A **20**, 4055 (some misprints of this paper have been corrected here).   see also:

Klafter, J. and Zumofen, G., 1994, J. Phys. Chem., **98**, 7366,

The general line of the presentation given here follows our work, which also contains an application to *subdiffusion of a plasma in a fluctuating (turbulent) magnetic field:*

Balescu, R., 1995, Phys. Rev., **E 51**, 4807.

Chapter 13

Critical Phenomena

13.1 Overview of the Equilibrium Critical Phenomena

We now study a problem that has been for a long time one of the great mysteries of statistical mechanics: the problem of PHASE TRANSITIONS and of CRITICAL PHENOMENA. The question arose first in the study of equilibrium properties. It is everybody's experience that matter exists in various states: solid, liquid, gas; it is also common knowledge that the transition from one state to another as temperature increases is an *abrupt* process, taking place at a well-defined temperature. A more detailed investigation shows that there exists a *critical temperature* above which this abrupt transition from liquid to gas disappears: the very distinction between a liquid and a gaseous state no longer exists. An even more quantitative study shows that certain thermodynamic quantities, such as the isothermal compressibility, become extremely large near the critical temperature: they nominally *diverge* at the critical temperature. The mystery is the following. Equilibrium statistical mechanics is, in principle, a completely solved problem. There exists a universal recipe: given the Hamiltonian of a system (which completely defines its dynamical properties at the microscopic level), the evaluation of the well defined *partition function* yields the free energy, hence all the thermodynamic quantities [see (3.29)]. The Hamiltonian of a system of interacting particles is a nice analytic function and the operations involved in the calculation of the partition function are smooth integrations. How can then discontinuities and divergences appear in the thermodynamic quantities at a certain value of the variables, which cannot be identified *a priori* in the Hamiltonian?

Another class of thoroughly investigated phenomena are those related to FERROMAGNETISM. When a piece of iron is submitted to a magnetic field H, it responds by producing a magnetic dipole moment, called the *magnetization*, M. The type of response is quite different in different temperature domains. At very high temperatures,

when the magnetic field is switched off, the magnetization returns to zero. Below a certain critical temperature (called the *Curie temperature*, T_c) there remains a *spontaneous magnetization*, M_0 when the external field H vanishes. The critical temperature is a point associated with a *spontaneous symmetry breaking* phenomenon. For $T > T_c$ a piece of iron is (macroscopically) isotropic: all directions are equivalent and the system is spherically symmetric. As the Curie temperature is crossed, there abruptly appears a privileged direction, marked by the spontaneous magnetization; the high degree of spherical symmetry changes to a lower cylindrical symmetry. This behaviour of the spontaneous magnetization is characteristic of a so-called *order parameter*. The critical point is also marked by divergences in a number of thermodynamic quantities, most notably the isothermal *magnetic susceptibility* $\chi = \partial M/\partial H$. The microscopic picture of a ferromagnetic substance is rather simple. Being a solid, it consists of a large collection of atoms located at the nodes of a crystal lattice. Each atom has a net spin, hence an individual magnetic moment; we henceforth call an atom possessing a spin simply "a *spin*". These spins interact with the external magnetic field H, but also with each other (each spin is a source of a magnetic field that interacts with the neighbouring spins through electromagnetic forces which must be described quantum-mechanically, thus producing the peculiar exchange interactions). The interactions and the magnetic field both tend to orient the spins parallel to each other, thus to produce a magnetization. This tendency is counteracted by the thermal agitation, which wins at high temperature. Below T_c, the thermal disorienting effect is overcome by the interactions, which are sufficiently strong to produce a magnetization even in the absence of an external field. An important quantity for the microscopic description of these systems is the *spin correlation function* $g(\mathbf{r}) = \langle \mathbf{s}(\mathbf{x})\mathbf{s}(\mathbf{x} + \mathbf{r}) \rangle$, which describes statistically the mutual influence of two spins separated by a distance $\mathbf{r}$. Like all correlation functions (see Chap. 4), this function introduces a characteristic length scale, usually denoted by ξ in this context, and called the *correlation length*. Its definition is analogous to Eq. (5.10): the correlation function is practically zero for distances $r \gg \xi$. It turns out that the correlation length tends to infinity as $T \to T_c$: this is another "mysterious" critical phenomenon.

Although this qualitative picture is clear, its implementation into a predictive theory has proved to be an extraordinarily difficult problem, for which a significant progress has been made only in the last three decades. The goal of a theory is not only the prediction of the qualitative features, such as the appearance of a spontaneous magnetization below T_c or the divergence of the susceptibility, but also a more quantitative determination of how exactly these phenomena behave. It has become customary to describe this behaviour by a set of *critical exponents* associated with various quantities. Thus, the spontaneous magnetization is described as follows as a function of the *reduced temperature* $\theta = (T - T_c)/T_c$:

$$M_0 \propto (-\theta)^\beta, \quad \theta < 0, \quad |\theta| \ll 1. \tag{13.1}$$

The power law, with the positive exponent β, describes the exact behaviour of M_0 below T_c (see Fig. 13.1.a). The behaviour of the susceptibility is described by two positive critical exponents (γ for $\theta > 0$, γ' for $\theta < 0$) (Fig. 13.1.b):

$$\chi \propto \begin{cases} \theta^{-\gamma}, & \theta > 0 \\ (-\theta)^{-\gamma'}, & \theta < 0 \end{cases} \tag{13.2}$$

The correlation length has a similar behaviour, with a critical exponent ν (Fig.13.1.c):[1]

$$\xi \propto \begin{cases} \theta^{-\nu}, & \theta > 0 \\ (-\theta)^{-\nu'}, & \theta < 0 \end{cases} \tag{13.3}$$
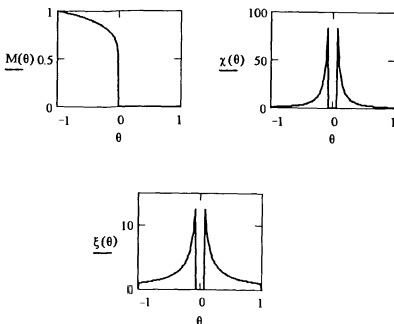

Figure 13.1. Critical behaviour in ferromagnetism.
Magnetization, Susceptibility, Correlation length.

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[1]Fig. 13.1 is drawn with the values of the critical exponents for the 2-dimensional Ising model: $\beta = 1/8$, $\gamma = 7/4$, $\nu = 1$.

One may add other critical exponents to this list. The critical exponents are measurable quantities (even though the necessary experimental techniques may be difficult). They are positive numbers, generally not integers. The purpose of a theory is not only to predict the numerical values of these exponents, a very stringent test indeed. It should also establish whether there exist *relations between the critical exponents*, hence to determine what is the minimum number of independent exponents. Last, but not least, we mention that the dynamical quantities (i.e., the transport coefficients) also have a peculiar behaviour near the critical point. These will, of course, be the main objects of interest in the present book.

We gave this brief review of the equilibrium properties of the ferromagnetic materials in the critical region as an introduction to the matter to be treated below.

13.2 Percolation

We study in the present chapter a problem which illustrates the critical phenomena in their simplest guise: the *percolation problem*. Since about 25 years this problem has been very intensively studied and an enormous amount of literature has been devoted to it. Curiously, however, it has not found its way in general textbooks of statistical mechanics. This is very strange, indeed, for various reasons. From a purely practical point of view, percolation is a very important tool for the study of equilibrium and transport properties of *disordered materials*, including such problems as the flow of liquids through porous materials, electrical conductivity of alloys of conducting and isolating substances, diffusion of charged particles in a turbulent plasma, and many others. From a theoretical point of view, it offers the simplest instance of a system displaying the whole range of critical phenomena. "Simplest" does not mean "trivial": most percolation problems cannot be solved analytically, and numerical simulation is an indispensable tool in this field. Finally, we may stress the intrinsic beauty of this problem, which makes connections with such fascinating fields of modern physics as strange transport, fractal geometry, etc.

The percolation problem is not described by a fundamental dynamical law: it rather appears as a *model* describing statistically in simple terms the behaviour of a very complex underlying dynamical system. It has therefore the same status as the random walk problems studied in the previous chapter. It can be said that its peculiar properties stem from a *mixture of probability and geometry*: it could also be characterized as a special chapter of STATISTICAL GEOMETRY. This statement will become clearer in the following developments.

The substrate of our system is a *lattice* imbedded in a space of d dimensions. Most often we consider a square lattice in two dimensions ($d = 2$). There exist, of course, other types of lattice (triangular, hexagonal,...); it will turn out that the dimensionality is a more important characteristic than the detailed structure. The

lattice may be finite (containing say, $N \times N$ sites), or infinite (thermodynamic limit). Each lattice site has z nearest neighbours. The value of z depends on the lattice structure and on the dimensionality; for a square lattice in two dimensions, $z = 4$. We now imagine that a certain number of "particles" are thrown *at random* on the lattice, and that, each particle may occupy one lattice site. It is assumed that the particles are independent of each other (no interactions). There are now two kinds of sites in the lattice: *occupied or unoccupied*. The lattice and its particles constitute our system. Its state is basically defined by a single variable p: *the occupation probability of an arbitrary site* (clearly, $1 - p$ is the probability that an arbitrary site is empty). Thus, $p = 0$ represents an empty lattice, $p = 1$ corresponds to a completely full lattice. The percolation problem is directly related to the CONNECTIVITY of the system: in this sense it is determined by the *geometrical or topological* properties of the system.

Consider a concrete example of a $N \times N$ lattice. The "particles" may represent atoms of a metallic substance, the "holes" could represent atoms of an insulating material: this is a model of an alloy mentioned above. What happens if we apply a potential difference between the upper and the lower limit of the crystal? We assume that a current can flow between two nearest neighbour sites if and only if they are both occupied. We say that two nearest neighbour sites belong to a CLUSTER if they are both occupied. On the contrary, an occupied site is *isolated* if all its nearest neighbours are empty. When the occupation probability p is very small, most particles are either isolated, or form small clusters (thus containing a finite number of particles). Clearly, no current can flow between the two limits of the lattice: the global system behaves like an *insulator*. As p increases, there appear on the average more and more clusters of larger size. When a certain value p_c is reached, there suddenly appears the possibility of a cluster connecting continuously the two limits: at this point a current can flow between the two limits. p_c is called the *percolation threshold* [2]. It is customary in the percolation literature to call this cluster the *infinite cluster* (even in a finite system!). For all values $p > p_c$ such a continuous path exists and the system behaves like an effective *conductor*. The suddenness of this change of properties strongly suggests an analogy with the ferromagnetic problem discussed in the previous section. The sudden appearance of an infinite cluster corresponds to the sudden appearance of a spontaneous magnetization when the temperature decreases and crosses the Curie temperature. The analog of the temperature is thus the variable $(1-p)$. The analogy is not accidental: we deal here with a *geometrical phase transition*

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[2]The problem defined here is called, more specifically, the "site percolation" problem. One can also define a "bond percolation" problem, in which the attention is drawn on the bonds rather than the sites. A given bond may be active or inactive (nothing is said here about the sites). The percolation threshold is reached whenever there appears a continuous path made of active bonds, connecting the extremes of the lattice. For a given dimensionality and a given lattice structure the thresholds for site percolation and for bond percolation are different ($p_c^{bond} < p_c^{site}$). We have not enough space for considering bond percolation in the present book.

occurring at a critical point and exhibiting all the characteristic *critical phenomena* which were identified in the physical phase transitions, as will presently be shown. It was recalled in the previous section that in a ferromagnet, the behaviour of the discontinuous quantities can be described, in the neighbourhood of the critical point, by power laws defining a set of *critical exponents*. The analogy with the percolation problem allows us to use the same notations for the critical exponents relative to analogous quantities.

Let P denote the *probability that an arbitrary site belongs to the infinite cluster*. This quantity is necessarily zero for all $p < p_c$, because an infinite cluster can only exist (by definition!) for $p \geq p_c$. This quantity has therefore the characteristic behaviour of an *order parameter*, like the spontaneous magnetization. It will be described by an equation analogous to (13.1):

$$P \propto (p - p_c)^\beta, \quad p > p_c. \tag{13.4}$$

where β is a positive number. The general behaviour of P is shown in Fig. 13.2.a, which is very similar to Fig. 13.1.a for the spontaneous magnetization. Another quantity of interest is the *average mass* (= the mean number of sites) of a *finite cluster*, S. Intuition tells us that in the undercritical region this quantity increases without limit as p grows from zero towards p_c (in the thermodynamic limit). In the supercritical region more and more sites belong to the infinite cluster, hence the mass of the finite clusters decreases. Thus, the behaviour of S is of the type shown in Fig. 13.2.b, which is quite analogous to the behaviour of the magnetic susceptibility shown in Fig. 13.1.b. The mass of the finite clusters is described, in the neighbourhood of the critical point, by a power law introducing the critical exponent γ:

$$S \propto |p - p_c|^{-\gamma}. \tag{13.5}$$

Finally, we consider the *correlation length*, ξ, defined as the *mean distance between two sites belonging to the same finite cluster* (a more precise definition will be given below). It is clear that ξ characterizes the linear size of the finite clusters; the qualitative argument discussed for the mass S applies here too and shows that the correlation length diverges at the critical point (Fig. 13.2.c):

$$\xi \propto |p - p_c|^{-\nu}, \tag{13.6}$$
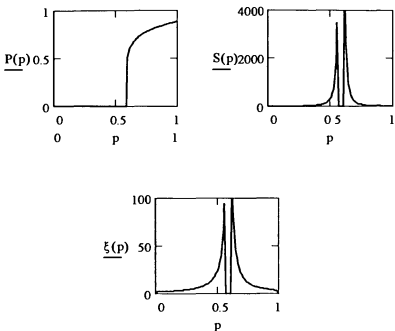
where $\nu > 0$ is a new critical exponent.

Figure 13.2. Critical behaviour in percolation

$$P(p), \quad S(p), \quad \xi(p)$$

Numerical simulations have shown that the critical exponents are *universal* quantities. This means that their value is independent of the structural details (such as the type of lattice): it only depends on the dimensionality d of the space. (For instance, for $d = 2$, the critical exponents are the same for a square lattice, a triangular one or a hexagonal one). On the contrary, the percolation threshold p_c does depend on these details. These are general properties of all *second order phase transitions*. The numerical values of these quantities for some interesting cases are collected in Table 13.1.

One could consider, of course, many more critical exponents, associated with other quantities. It turns out, however, that there exist (fortunately!) many relations among these exponents. It will be shown, in particular, that for the static properties considered here, only *two* critical exponents are independent: all the others are determined by these two.

d		p_c	β	γ	ν	σ	τ	μ
1		1		1	1			
2	square	0.5927	5/36	43/18	4/3	36/91	187/91	1.30
	triang	0.5000						
	hexagon	0.6962						
3	simp cub	0.3116	0.41	1.80	0.88	0.45	2.18	2.0
	BCC	0.246						
	FCC	0.198						
-	Bethe	$(z-1)^{-1}$	1	1	1/2	1/2	5/2	3

Table 13.1. Percolation thresholds and critical exponents

13.3 One-dimensional Systems

It was stated before that most percolation problems cannot be solved analytically. The very few ones that can be solved therefore provide us with a very useful guide for assumptions about the general case: these assumptions must then be tested numerically. The simplest exactly soluble system is a *one-dimensional chain*. A *cluster* in this system is a group of connected occupied sites, with the condition that the sites neighbouring the extreme left and the extreme right site are empty (Fig. 13.3).

Clearly, in one dimension, the only possibility for connecting the extremes by a continuous path of neighbouring occupied sites is that *all* sites are occupied. Hence, the percolation threshold is: $p_c = 1$, which is the limit of the physical domain of p. The one-dimensional chain is thus somewhat degenerate: there exists no supercritical region.[3] We may, however, calculate some interesting physical quantities.

An important quantity is the *correlation function*, $g(r)$. It is defined as the *probability that a site at distance r from an occupied site is also occupied and belongs to the same cluster*. For $d = 1$, this quantity is easily obtained. For $r = 1$, the neighbouring site belongs to the cluster only if it is occupied; it can, however, be located to the right or to the left of the origin, hence, $g(1) = 2p$. For $r > 1$, this site, and all intermediate $r - 1$ sites must be occupied, hence:

$$g(r) = 2p^r. \tag{13.7}$$

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[3]It should be recalled that the partition function of the well-known Ising model in one dimension, i.e., a chain of spins capable of two orientations (up or down) and interacting with their nearest neighbours, can also be solved exactly. It presents the same kind of degeneracy: a spontaneous magnetization appears only when the temperature is exactly zero: $T_c = 0$.

The correlation function allows us to define precisely the correlation length as the root mean square distance between two sites on the same cluster; because of the simple form of Eq. (13.7) this quantity is easily calculated by summing geometric series:

$$\xi^2 = \frac{\sum_{r=1}^{\infty} r^2 g(r)}{\sum_{r=1}^{\infty} g(r)} = \frac{\sum_{r=1}^{\infty} r^2 p^r}{\sum_{r=1}^{\infty} p^r} = \frac{1+p}{(1-p)^2} \approx \frac{1+p}{(p_c - p)^2}, \tag{13.8}$$

where we recalled that $p_c = 1$. The singularity of the correlation length is thus described by the following equation, defining the critical exponent ν:

$$\xi \propto |p_c - p|^{-\nu}, \quad \nu = 1. \tag{13.9}$$

This result allows us to derive the asymptotic form of the correlation function, for large distances and in the neighbourhood of the percolation threshold. From Eq. (13.7), using again $p_c = 1$, we find:

$$\ln g(r) = \ln 2 + r \ln p = \ln 2 + r \ln [1 - (p_c - p)] \approx \ln 2 + r [- (p_c - p)]$$
$$\approx \ln 2 - r \cdot \frac{1}{\xi}.$$

Hence, for $(p_c - p) \ll p_c$ and $r \gg \xi$, we find:

$$g(r) \propto \exp\left(-\frac{r}{\xi}\right). \tag{13.10}$$

This exponential decay of the correlation function shows that, in the subcritical region, ξ is a characteristic length measuring the typical size of the (finite) clusters. At the percolation threshold $\xi \to \infty$: the condition $r \gg \xi$ can no longer be satisfied and Eq. (13.10) is no longer valid. This case will be discussed in the next section.

We leave as an exercise for the reader the following calculation of the mean mass of a finite cluster, obtained by summing the occupation probabilities of successive sites starting from the (occupied) origin:

$$S = 1 + \sum_{r=1}^{\infty} g(r) = \frac{1+p}{p_c - p}: \quad \gamma = 1. \tag{13.11}$$

We now introduce a quantity playing a fundamental role in (static) percolation theory, because all other relevant quantities can be related to it. This is $\tilde{n}_s(p)$: the *probability that a chosen lattice site belongs to a cluster of s sites.* This probability is built up from three factors (see Fig. 13.3): p^s (probability of occupancy of s sites), $(1-p)^2$ (because the two sites neighbouring the extremes must be empty),

and s (because the chosen site may be any one of the sites of the cluster); thus $\bar{n}_s(p) = sp^s(1-p)^2$.

Figure 13.3. Clusters on a 1D lattice.

Most often one considers instead of $\bar{n}_s(p)$ the *probability per cluster site*: $n_s(p) = \bar{n}_s(p)/s$:

$$n_s(p) = p^s(1-p)^2. \qquad (13.12)$$

We now write this quantity in a form appropriate for the neighbourhood of the percolation threshold [recalling that $p \leq 1$, hence $\ln p \leq 0$, and that $p_c = 1$]:

$$
\begin{aligned}
n_s(p) &= (1-p)^2 \exp\left[-s\left|\ln p\right|\right] = (1-p)^2 \exp\left\{-s\left|\ln\left[1+(p-p_c)\right]\right|\right\} \\
&\approx (1-p)^2 \exp\left\{-s\left|p-p_c\right|\right\} = s^{-2} \, s^2 \left|p-p_c\right|^2 \exp\left\{-s\left|p-p_c\right|\right\}.
\end{aligned}
$$

We may thus write this quantity in the following form:

$$n_s(p) = s^{-\tau} f(x), \qquad x = (p-p_c)\, s^\sigma \qquad (13.13)$$

[annotation: $\tau = 2$]

This is called a *scaling relation*[4]. It tells us that the probability $n_s(p)$, a function of the two variables s and p, appears as a product of two factors. It contains a *prefactor* which is a power of s alone, and a function depending only on the *similarity variable* x. In other words, $f(x)$ depends on s and on p only through the combination $x = (p-p_c)\, s^\sigma$. For the systems under consideration ($d=1$), $f(x) = x^2 \exp(-x)$. Eq. (13.13) introduces two exponents which, for one-dimensional systems, have the values: $\tau = 2$, $\sigma = 1$. The importance of the scaling relation (13.13) will appear in the next section. It will be shown, in particular, that all the relevant critical exponents are expressed in terms of σ, τ and the dimensionality d.

13.4   Scaling Theory of Percolation

Eq. (13.13) was derived analytically from an exact relation for one-dimensional systems. Unfortunately, as soon as we consider dimensionalities $d \geq 2$, it becomes impossible to solve the percolation problem exactly. In order to realize where the

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[4]We have met with scaling relations previously, in the theory of continuous time random walks, see Eq. (12.64).

main difficulty appears, consider a square lattice in two dimensions, and try to determine the probability $n_s(p)$. This quantity will involve again a factor p^s for a cluster with s occupied sites, and a second factor expressing that all the sites around the periphery must be empty: $(1 - p)^t$. The value of t depends on the *shape* of the cluster (see Fig. 13.4).

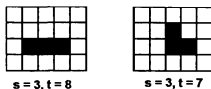s = 3, t = 8   s = 3, t = 7

Figure 13.4. Two shapes for 3-clusters.

We must thus first enumerate, for each value of s, the various possible shapes of clusters (these are often called *animals*) and determine the value of t for each of them. In one dimension this gives a factor s, see the expression of $\bar{n}_s(p)$; in higher dimensions we must determine a number of configurations (per cluster site) $g_{s,t}$ taking into account the various orientations of the animals. For our example, the straight animal yields $g_{3,8} = (6/3) = 2$, whereas the bent animal yields $g_{3,7} = 12/3 = 4$ (Fig. 13.5). Clearly, for larger clusters and higher dimensions, the determination of all the animals, hence of the index t, and the counting process resulting in the coefficient $g_{s,t}$ pose a formidable combinatorial problem, which make the percolation problem insoluble analytically.
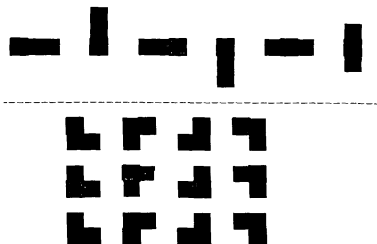
Figure 13.5. Counting of animals

There is only one other system which can be treated exactly: the *Bethe lattice*, also called the *Cayley tree*. It consists of an arrangement in which each site has $z > 2$ neighbours arranged like a star with z branches of unit length[5]; any two sites are connected by a single path (there are no loops). We have unfortunately no space for deriving in detail the results for the Bethe lattice. Let us just say here that in this case there is a non-trivial percolation threshold: $p_c = (z - 1)^{-1}$. Next, it is easily seen that for every s there is a single animal, and that t is entirely determined by s [one finds that $t = z + (s - 1)(z - 2)$]. The probability (per cluster site) $n_s(p)$ that a given site belongs to a cluster of size s can now be determined exactly. It appears that, for $p \to p_c$, it has the scaling form (13.13), with values of σ, τ given in Table 13.1; from these, the other critical exponents can be calculated exactly.

These results for the Cayley tree played an important historical role. When the connection between percolation and the theory of critical phenomena was clearly realized, the specialists of the former were influenced by the great progress in the latter theory that occurred around the seventies. The introduction of a scaling assumption by Widom in the theory of ferromagnetism (which provided a non-trivial correction to the classical phenomenological Landau theory), the appearance of the concepts of universality and of self-similarity in Kadanoff's work, crowned by Wilson's formulation of the renormalization group were essential milestones in the development of the

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[5]For $z = 2$, the Cayley tree reduces to the one-dimensional chain.

theory of critical phenomena. Given the exact results obtained for $d = 1$ and for the Bethe lattice, it was natural to apply them to percolation theory. The result will be briefly outlined below.

The theory starts with a bold generalization of Eq. (13.13) or, more precisely, of its domain of validity:

SCALING HYPOTHESIS: *The probability (per cluster site) that a given site belongs to a s-cluster is given, for all dimensionalities and all lattice structures, by a scaling form involving two characteristic exponents:*

$$n_s(p) = s^{-\tau} f_\pm \left[|p - p_c|^{1/\sigma} s \right] \qquad (13.14)$$

This form is assumed to be valid for $p \to p_c$ and $s \to \infty$. The exponents σ, τ are universal (they only depend on the dimensionality d) and have the same value below and above the percolation threshold. The notation $f_\pm(x)$ denotes two functions: $f_+(x)$ is defined for $x > 0$ (i.e., $p > p_c$), and $f_-(x)$ for $x < 0$. These functions cannot be specified a priori: their form is not universal (it depends on the lattice structure). There exists a cross-over size $s_\xi = |p - p_c|^{-1/\sigma}$ such that:

$$
\begin{aligned}
f_\pm(x) &\to \text{const}, && \text{for } |x| \ll 1, \quad \text{i.e., } s \ll s_\xi, \\
f_\pm(x) &\to 0 \text{ (very fast)}, && \text{for } |x| \gg 1, \quad \text{i.e., } s \gg s_\xi.
\end{aligned} \qquad (13.15)
$$

The first of these statements implies that at the percolation threshold, $n_s(p)$ has a power law behaviour:

$$n_s(p) \sim s^{-\tau} \qquad (13.16)$$

It should be clear that these statements cannot be derived in any rigorous way from first principles[6][7]. They have, however, been very extensively checked by numerical simulations and found to be surprisingly accurate. The few cases where there appear deviations can be explained by natural generalizations of Eq. (13.14). We now show how the various critical exponents can be derived from the scaling form, without a precise specification of the scaling function $f_\pm(x)$. We first need a few lemmas.

For $p < p_c$ the probability for an occupied site to belong to a (finite) cluster of size s is $\hat{n}_s(p) = s n_s(p)$ (including isolated sites, which are clusters of size $s = 1$). Thus,

---

[6]The scaling form can be derived by an application of the renormalization group. Although this leads to a very elegant formulation, it displaces the problem: the applicability of the renormalization group to this problem is also an unprovable assumption.

[7]We may recall that our first meeting with a scaling law was in the problem of continuous time random walks, more specifically, the SLT-CTRW. The density profile is given by Eq. (12.64), which was derived from an exact asymptotic theory.

an occupied site (which has probability p) belongs either to a cluster of size $s = 1$, or to a cluster of size $s = 2$, etc. Thus:

$$\sum_s s n_s(p) = p, \quad p < p_c. \tag{13.17}$$

In the critical or supercritical regime, one must also take into account the infinite cluster. Thus any occupied site belongs either to the infinite cluster (with probability P), or to a finite cluster; as a result:

$$P + \sum_s s n_s(p) = p, \quad p > p_c. \tag{13.18}$$

We now calculate the mass of the finite clusters for $p \to p_c$, obtained as the size s, averaged with $\bar{n}_s(p) = s n_s(p)$:

$$
\begin{aligned}
S &= \frac{\sum_s s \cdot s n_s(p)}{\sum_s s n_s(p)} \approx \frac{1}{p} \int ds\, s^2 s^{-\tau} f_\pm \left(|p - p_c|^{1/\sigma} s \right) \\
&\approx |p - p_c|^{-(3-\tau)/\sigma} p_c^{-1} \int dx\, x^{2-\tau} f_\pm(x).
\end{aligned}
$$

In the second step we used (13.16)[8] and approximated the sum by an integral; next, we approximated p by p_c and made the substitution $s \to x = |p - p_c|^{1/\sigma} s$ in the integrand. This is the main step, which allows us to obtain the explicit dependence of S on $|p - p_c|$; the remaining integral is just a number (if it converges!). Thus:

$$S \sim |p - p_c|^{-\gamma}, \quad \gamma = \frac{3-\tau}{\sigma}, \quad |p - p_c| \ll p_c. \tag{13.19}$$

In order to calculate the exponent β we use Eq.(13.19), which we combine with (13.17) for $p = p_c - \varepsilon$ in order to ensure convergence:

$$
\begin{aligned}
P &= p - \sum_s s n_s(p) + \sum_s s n_s(p_c) - p_c \\
&\approx \int ds\, s \left[n_s(p) - n_s(p_c) \right] + (p - p_c) \\
&= \int ds\, s^{1-\tau} \left[f_\pm \left(|p - p_c|^{1/\sigma} s \right) - 1 \right] + (p - p_c) \\
&\approx \int ds\, s^{1-\tau} s |p - p_c|^{1/\sigma} f'_\pm \left(|p - p_c|^{1/\sigma} s \right) + (p - p_c) \\
&= |p - p_c|^{-(2-\tau)/\sigma} \int dx\, x^{2-\tau} f'(x) + (p - p_c).
\end{aligned}
$$

---

[8]Note that, even for $p \geq p_c$, the infinite cluster must not be included in this calculation, by definition of S.

Thus, the dominant behaviour near p_c is:

$$P \propto |p - p_c|^\beta, \quad \beta = \frac{\tau - 2}{\sigma}. \tag{13.20}$$

[This result requires that $\frac{\tau-2}{\sigma} < 1$, a condition that turns out to be always satisfied (see Table 13.1)]. By rearranging Eqs. (13.19) and (13.20), the exponents σ, τ can be expressed in terms of β, γ:

$$\sigma = \frac{1}{\beta + \gamma}, \quad \tau = 2 + \frac{\beta}{\beta + \gamma}. \tag{13.21}$$

By using the same type of arguments, we derive a general formula for the moment of order k (not necessarily an integer!) of the probability distribution $n_s(p)$:

$$M_k = \sum_s s^k n_s(p) \approx \int ds \, s^{k-\tau} f_\pm \left(|p - p_c|^{1/\sigma} s \right)$$
$$\propto |p - p_c|^{(1-k+\tau)/\sigma} \tag{13.22}$$

This result exhibits the great interest of the scaling assumption. *The critical exponents relative to any quantity expressible as a moment of n_s can all be expressed in terms of the two exponents τ, σ, independently of the form of the scaling function $f_\pm(x)$.* Alternatively, any one of the critical exponents can be expressed in terms of two of them, e.g. β, γ.

13.5 Percolation Clusters and Fractals

We still need an important critical exponent, ν, related to the correlation length ξ. This quantity is rather different from, say, S or P, because it involves the idea of distance, hence of spatial structure.

The correlation length was clearly defined in Eq. (13.8) in the correlation function $g(r)$; we now need to relate the latter quantity to $n_s(p)$, for which we know the scaling form. $g(r)$ was defined in Sec. 13.3 as the probability that a site at distance r from an occupied site is itself occupied and belongs to the same cluster. Thus, the average number of sites to which an occupied site is connected is $\sum_r g(r)$; this quantity can also be expressed as $\sum_s s \cdot s n_s/p$ since $s n_s/p$ is the probability that an occupied site belongs to a cluster of s (connected) sites. Thus:

$$\sum_s s^2 n_s = p \sum_r g(r) \tag{13.23}$$

Because of this relation, we can express the correlation length in two ways, one involving the correlation function and a sum over r [i.e., Eq. (13.8)], and another one expressed in terms of the size s of the clusters:

$$\xi^2 = \frac{\sum_r r^2 g(r)}{\sum_r g(r)} = \frac{\sum_s R_s^2 s^2 n_s}{\sum_s s^2 n_s} \qquad (13.24)$$

Here R_s^2 is the square of the *gyration radius*, i.e., the squared distance between two sites in a s-cluster, averaged over all such clusters; recalling that the number of pairs of sites in a s-cluster is $s(s-1)/2$, we find: Эгого и Пока не поняла

$$R_s^2 = \frac{1}{s(s-1)/2} \sum_{i=1}^{s} \sum_{j=1}^{i} |\mathbf{r}_i - \mathbf{r}_j|^2. \qquad (13.25)$$

In order to determine the dependence of R_s on s, we appeal to a quite general argument. In the neighbourhood of the percolation threshold the large clusters and the infinite cluster are not homogeneous structures, but have a large number of holes of many sizes: this is characteristic of a *fractal structure*. Such a structure introduces the concept of *fractal dimension* defined (somewhat loosely) by considering the mass of the cluster included within a sphere of radius r (in d dimensions), $m(r)$. If the cluster were homogeneous (i.e., if the density were constant), this quantity would be proportional to the volume of the sphere, i.e., $m(r) \sim r^d$. But, because of the holes, the mass is smaller; it therefore introduces a *fractal dimension*, $d_f < d$, defined as follows:

$$m(r) \sim r^{d_f} \qquad (13.26)$$

This is just a definition; the remarkable fact shown below is that the fractal dimension d_f is expressed in terms of the same basic numbers σ, τ as all the other critical exponents. Before doing this, we go back to Eq. (13.24). We note that (13.26) implies that the number of sites within a sphere of radius r: $s(r) \sim r^{d_f}$; it then follows that:

$$R_s \sim s^{1/d_f} \qquad (13.27)$$

Substituting this into (13.24), we see that the correlation length is now simply expressed as a ratio of two moments of n_s, which can be evaluated by the general result (13.22):

$$\xi^2 = \frac{M_{2+(2/d_f)}}{M_2} = \frac{|p - p_c|^{(1+\tau-2-(2/d_f))/\sigma}}{|p - p_c|^{(1+\tau-2)/\sigma}} = |p - p_c|^{2/\sigma d_f}$$

We thus find:

$$\xi \propto |p - p_c|^{-\nu}, \quad \nu = \frac{1}{\sigma d_f}. \qquad (13.28)$$

This formula is valid in all regimes; it is important to note the interpretation of this quantity. Below the threshold, ξ is a measure of the mean size of the (finite) clusters; above the threshold it measures the mean size of the holes in the infinite cluster. It must be stressed that, for $p > p_c$, the correlation length defines a *cross-over length*. This is understood as follows. At $p = p_c$, ξ is infinite, any length is smaller than ξ! In other words, there is no characteristic length in the problem: this is the origin of the fractal structure of the infinite cluster. As p grows above the threshold, ξ decreases again. It then follows that for length scales much smaller than ξ, $r \ll \xi$, the situation looks similar to the critical threshold: the cluster is fractal. But for $r \gg \xi$, the fractal structure is wiped out: the cluster looks homogeneous. This is expressed by the following relation for the mass contained in a circle of radius r:

$$m(r) \sim \begin{cases} r^{d_f}, & r \ll \xi \\ r^d, & r \gg \xi \end{cases} \qquad (13.29)$$

This property allows us to relate the fractal dimension to the critical exponents. Consider, for $p > p_c$, a circle of radius $r < \xi$ lying within the circle belongs to the infinite cluster is P; this is also the ratio between the number of sites (within the circle) belonging to the infinite cluster and the total number of sites within the circle. This relation is true for $r = a\xi$, with $a < 1$:

$$P \propto \frac{r^{d_f}}{r^d}.$$

From the definitions (13.4) and (13.6) we find:

$$|p - p_c|^\beta \propto |p - p_c|^{-\nu(d_f - d)},$$

hence:

$$d_f = d - \frac{\beta}{\nu}. \qquad (13.30)$$

We now combine this equation with (13.28) and find $\nu d - \beta = \sigma^{-1}$; using (13.20), we find an explicit definition of ν in terms of the basic critical exponents:

$$\nu = \frac{\tau - 1}{d\sigma}. \qquad (13.31)$$

When this result is combined with (13.28), we find the relation between fractal and normal dimensions:

$$d_f = \frac{d}{\tau - 1}. \qquad (13.32)$$

These results allow us to write the scaling relation (13.14) in a very interesting form. In the similarity variable $z = |p - p_c|^{1/\sigma} s$ we may use ξ instead of $|p - p_c|$ through Eq. (13.28), thus:

$$|p - p_c|^{1/\sigma} = \xi^{-(1/\nu\sigma)} = \xi^{-d_f}.$$

The scaling relation thus becomes:

$$n_s(p) \propto s^{-\tau} f_{\pm}\left(\frac{s}{\xi^{d_f}}\right). \tag{13.33}$$

Alternatively, this can also be written as:

$$n_s(p) \propto \xi^{-\tau d_f} F_{\pm}\left(\frac{s}{\xi^{d_f}}\right) \tag{13.34}$$

with $F_{\pm}(y) = y^{-\tau} f_{\pm}(y)$.

The problems discussed in the present and the previous sections are related to the static percolation phenomena: they are, in principle, outside the mainline of the present book. They do, however, constitute a necessary introduction to the study of non-equilibrium phenomena. The concepts of critical exponents and the scaling laws will appear as basic ingredients of the latter phenomena as well. We stress again the fact that the scaling assumption has never been derived from first principles. It has, however, been remarkably verified in all numerical simulations performed to date. There exists a derivation from a more fundamental concept (the behaviour under a certain group of symmetry transformations, essentially related to the group of dilatations, thus of changes of scale). This *renormalization group theory*, pioneered by K. Wilson in 1971, was a great step in the history of the theory of critical phenomena. Whereas it is a remarkable synthesis of the problems, it is also based on some reasonable, but unproved assumptions. We have no space here for a discussion of the renormalization group approach, for which there exists an abundant literature, and we rather go over to the main subject of our book: transport properties.

13.6   Bibliographical Notes BN13

The best introduction to equilibrium "thermal" critical phenomena (in particular, related to ferromagnetism) remains:

Stanley, H.E., 1971, *Introduction to Phase Transitions and Critical Phenomena*, Oxford Univ. Press.

For the more recent developments (based, in particular on the renormalization group), see:

Balescu, R., 1975: RB-2 (BN1),

Ma, S.K., 1976, *Modern Theories of Critical Phenomena*, Benjamin, New York.

From the extensive literature on percolation, we extract a remarkable "semi-popular" paper:

de Gennes, P.G., 1976, La Recherche, **7**, 919,

a collection of excellent papers:

Deutscher, G. Zallen, R. and Adler, J. (editors), 1983, *Percolation Structures and Processes*, A. Hilger, Bristol,

and an excellent book on the general theory (with many references):

Stauffer, D. and Aharony, A., 1992, *Introduction to Percolation Theory*, (2nd ed.), Taylor and Francis, London.

The exact solution of the percolation problem on the *Bethe lattice* was obtained in a classical work on polymers:

Flory, P.J., 1941, J. Amer. Chem. Soc., **63**, 3091.

The theory of *fractals* and some of its applications to percolation is found in:

Mandelbrot, B.B., 1982, *The Fractal Geometry of Nature*, Freeman, San Francisco,

Mandelbrot, B.B. and Given, J.A., 1984, Phys. Rev. Lett., **52**, 1853,

Zel'dovich, Ya.B. and Sokolov, D.D., 1985, Sov. Phys. Usp., **28**, 608.

The *scaling assumption* was introduced by:

Widom, B., 1965, J. Chem. Phys., **43**, 3829, 3898; see also:

Kadanoff L.P. *et al.*, 1967, Rev. Mod. Phys., **39**, 395.

The *renormalization group (RNG)* theory of critical phenomena was introduced in a series of three (Nobel-prize winning) papers:

Wilson, K.G., 1971, Phys. Rev., B **4**, 3174, 3184,

Wilson, K.G. and Fisher, M., 1972, Phys. Rev. Lett, **28**, 240.

Many applications of the *RNG to percolation* problems are found in:

Bouchaud, J.Ph. and Georges, A., 1990, (BN12).

Chapter 14

Transport on Percolation Structures

14.1 Electrical Conductivity and Percolation

At the beginning of Sec. 13.2 we introduced the idea of percolation through the concrete example of the electrical conductivity of an alloy of a conducting and an insulating material. We now discuss this problem in more detail.
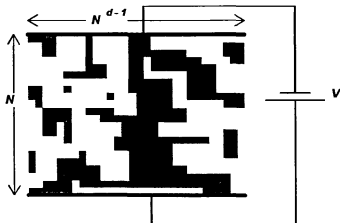

Figure 14.1. Conductance in disordered alloy.

We first define the geometry of our situation. The sample of alloy under consideration consists of a lattice in d-dimensional space, bounded by two parallel plane

metallic plates separated by a distance L in the x-direction (Fig. 14.1). There are N sites in a direction perpendicular to x; then the area of the metallic plates is proportional to N^{d-1}. A voltage V is applied between the two plates, and the current J in the x-direction is measured. Assuming a linear transport equation: $J = \bar{\Sigma} V$, we define $\bar{\Sigma}$ as the *conductance* of the sample. This quantity depends on the geometry: it is proportional to the area of the plates and inversely proportional to the distance between them; thus:

$$\bar{\Sigma} = \frac{N^{d-1}}{L} \Sigma.$$

The *electrical conductivity* Σ no longer depends on the size and shape of the sample, but it does depend on the composition. We make the convention of calling a site *occupied* if it is occupied by an atom of conducting material, and calling it *empty* if it is occupied by an atom of insulating material; we denote, as usual, by p the probability that a given site is occupied. Clearly, $\Sigma(0) = 0$, and $\Sigma(1) = 1$ (the conductivity being normalized in such a way that it equals 1 for the pure conducting material). It is also clear that for $p \ll 1$ there is no continuous path connecting the two end plates, hence there is no current, and $\Sigma(p) = 0$. It is only when the infinite cluster appears, i.e., at $p = p_c$, that the current can flow. One would thus expect that the conductivity $\Sigma(p)$ would have the same behaviour as the probability of belonging to the infinite cluster, $P(p)$. In particular, the two quantities should be described by the same critical exponent: $\Sigma(p) \propto |p - p_c|^\beta$. It turned out, however, from a real experimental study of Last & Thouless (1971) that this is not at all the case. Instead, one finds the following relation, valid for a sufficiently large size, $L \gg \xi$:

$$\Sigma(p) \propto |p - p_c|^\mu, \quad p > p_c. \tag{14.1}$$

The *non-equilibrium exponent* μ ($\mu > 0$) is quite different from β (see Table 13.1 and Fig. 14.2): it turns out that it cannot be related to any of the static exponents (although the threshold is the same).
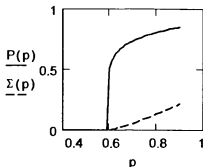
Figure 14.2. Critical behaviour of P(p) and Σ(p).

On second thought, the reason of this difference appears quite clearly. If we look at the "infinite" cluster (Fig. 14.3) we note that there is a continuous path connecting top and bottom, called the *backbone* of the cluster, onto which are "grafted" many sidepaths that can be considered as dead ends, because they do not reach the extreme plates. When a voltage is applied, the current flows only along the backbone: there is no current in the dangling bonds. Thus, only the backbone counts in a study of the conductivity: the dangling bonds may be deleted. What is left is again a fractal, like the whole infinite cluster, but clearly with a different fractal dimension. Till now, nobody has found an exact relation between these two fractal dimensions, hence the nonequilibrium exponent μ appears as a new independent basic exponent.

Figure 14.3. Backbone and dangling bonds

In order to study the conductivity problem more deeply, we need a true transport theory in percolation structures, rather than a mere phenomenological relation through a critical exponent, like (14.1). In order to attack this problem, we recall a well-known relation in statistical mechanics, due to Einstein: the electrical conductivity Σ of a metal (or a plasma) is proportional to the diffusion coefficient $\mathcal{D}$ of the electrons. This relation was derived in Chap. 11, Eq. (11.69). De Gennes (1976) accepted this relation for random resistors as well[1]. It then follows that the diffusivity has the same behaviour as the conductivity:

$$\mathcal{D} \propto |p - p_c| \,. \tag{14.2}$$

One can then take advantage of the relation between diffusion and stochastic processes (in particular, random walks, i.e., the matters treated in Chap. 12) in order to study dynamical (or "semi-dynamical") models of transport. We thus introduce the *TIME* as a new variable in our non-equilibrium study.

14.2   Diffusion and Percolation

We have studied in Chap. 12 the relation between diffusion and random walks. It was shown there that certain types of random walk may lead to *strange diffusion*. We now define a random walk that describes diffusion in presence of a percolative structure, i.e., a disordered medium. This problem was first introduced by de Gennes in 1976 with the very picturesque name of the "*ant in a labyrinth*".[2] The model describes a discrete time random walk of a point particle (the *ant*) on a lattice (in d dimensions), with an additional constraint (which makes the difference with a classical random walk). The lattice is the host of a percolative structure: its sites are either "occupied" - with probability p - or "empty"[3], the occupied sites are distributed at random, without any correlation. The constraint is the following: the ant can only make individual jumps from an occupied site to a nearest neighbour site *that is also occupied*. The walk is then defined as follows. At time $t = 0$, the ant starts from an occupied site and attempts to move by choosing at random one of its nearest neighbours: if the latter is occupied, the ant moves to that site; if it is empty, the ant remains at its initial position. At time $t = 1$, the process is repeated, and so on. After a time t we measure the square of the distance $r^2(t)$ from the ant's position

---

[1] This assumption is rather strong. Some authors attempted to give a real proof of the Einstein relation for disordered materials.

[2] It should be realized that the problem described here is not the only one relating diffusion and percolation. Other models will be presented in the present and the next section, that are related to different aspects of this theme.

[3] It is not necessary to define whatever is "occupying" the sites. The attribute "occupied" is merely a tag allowing to distinguish two types of sites.

at this time and its initial position. The process is then repeated by starting from another initial position. The quantity of interest is the mean square displacement (MSD) $\langle r^2(t) \rangle$, averaged over the initial positions, for given lattice and given p: this quantity is related to diffusion, as we know from Chap. 12. To simplify the notation we use the symbol: $R(t) \equiv \langle r^2(t) \rangle^{1/2}$.

What can be expected qualitatively from such a model? When $p = 1$, the constraint disappears: all the sites are accessible, and the ant performs a classical random walk on a lattice, leading to a diffusive process [see Eqs. (12.18) or (12.29)]:

$$R^2(t) = 2d\,\mathcal{D}\,t, \quad p = 1. \tag{14.3}$$

In the opposite limit, $p = 0$, the ant cannot move at all. Consider now a small value of p, below the percolation threshold, $p < p_c$: in this case there are only finite clusters on the lattice. An ant starting in a given cluster can never leave it. Thus, the MSD cannot grow indefinitely in time as in (14.3); rather, the MSD tends asymptotically to a constant value as $t \to \infty$:

$$R^2(t) \to const, \quad p < p_c. \tag{14.4}$$

When the percolation threshold is reached or/and crossed, there appears an infinite cluster. An ant starting on it has the possibility of moving arbitrarily far from its starting point, thus $R^2(t)$ can grow indefinitely in time. We may, however, expect a *subdiffusive behaviour* for two reasons:

• There are still finite clusters present: these act as traps for any ants starting on one of them;

• On the infinite cluster there are holes and dangling bonds, i.e., dead ends: the infinite cluster looks indeed like a labyrinth for the poor ant trying to find its way out!

As a result the dispersion of the ants is slower than in a diffusive process. We may thus write a relation similar to (12.62) for long (but not VERY long!) time:

$$R^2(t) = B\,t^\alpha, \quad p_c \le p \le 1. \tag{14.5}$$

THE DIFFUSION EXPONENT $\alpha = \alpha(p)$ is a function of p (and of the dimensionality d). [4] Numerical simulations have shown that, at the percolation threshold, $\alpha(p_c) \approx 2/3$ for $d = 2$, and $\alpha(p_c) \approx 0.4$ for $d = 3$; clearly, $\alpha(p) \to 1$ as $p \to 1$. It should now be noted that the subdiffusive behaviour is actually a "semi-asymptotic" result.

---

[4] There is, unfortunately, no agreement about a unified notation for the diffusion exponent. Stauffer and Aharony, for instance, use the notation: $R(t) \sim t^k$, hence $k = \alpha/2$. Other definitions also appear in the literature.

Actually, when the MSD has grown sufficiently large, the ant distribution no longer feels the fractal details, and the diffusion exponent tends to 1 as $t \to \infty$. The cross-over from subdiffusive to diffusive behaviour occurs for a characteristic time t_c. At first sight, one would think that it is provided by the correlation length ξ: whenever the MSD at time t is smaller than ξ^2, the regime is subdiffusive. Thus, t_c would be defined implicitly by the relation:

$$R^2(t_c) \stackrel{?}{=} \xi^2 \tag{14.6}$$

It will be seen, however, at the end of this section, that this definition of t_c is not correct.

At this point we may introduce a remark on terminology. The final diffusive regime in this problem is characterized by a coefficient $\mathcal{D}$ depending on p. It should be stressed that the diffusion mechanism in the percolation problem is completely different from the collisional mechanism on which the classical transport theory of Chap. 10 is based. The diffusion results from the ant's progressively finding her way through the labyrinth. It is therefore determined by the connectivity of the system, i.e., a global or collective property. This is clearly expressed by the fact that the diffusion coefficient depends on p, which measures the degree of disorder of the system. We propose the following definition:

ANOMALOUS DIFFUSION *is defined as a process that is* diffusive *($\alpha = 1$), but with a diffusion coefficient depending on* variable(s) unrelated to collisions, *characterizing the degree of disorder or randomness of the medium.*

This definition introduces a clear distinction between this type of process and the non-diffusive regimes ($\alpha \neq 1$), which we called STRANGE DIFFUSION, but which are also called "anomalous diffusion" by a majority of authors. Anomalous diffusion (in our sense) is, on the other hand, a well accepted and widely used terminology in turbulent hydrodynamics, plasma physics, etc. In such cases the anomalous diffusion coefficient depends on the intensity of the fluctuations, which are again a measure of the degree of randomness, or disorder of the system. We believe that a clear distinction between these two widely different concepts is highly desirable.

We now sum up the situation described above as follows.

$p < p_c$			$\alpha(p) = 0$
$p = p_c$	$d = 2$		$\alpha(p_c) \approx 2/3$
	$d = 3$		$\alpha(p_c) \approx 0.4$
$p > p_c$		$1 \ll t \ll t_c$	$\alpha(p_c) < \alpha(p) < 1$
		$t \gg t_c$	$\alpha(p) \approx 1$
$p = 1$			$\alpha(1) = 1$

$$\tag{14.7}$$

The evolution of the ant density profile can be described by a gain-loss equation of the general form (9.11), by defining transition probabilities between sites in agreement with the constraints. Such an equation is necessary for the numerical simulations. Many interesting results can, however, be obtained by a straightforward application of the concepts of percolation theory developed in the previous chapter.

Consider first the subcritical case, $p < p_c$. For long times, the MSD for an ant starting in an s-cluster saturates at a value R_s, i.e., the characteristic size of the cluster. The latter depends on s as in Eq. (13.27); averaging this result with the probability $s n_s(p)$ we find, for $t \to \infty$:

$$R_\infty^2 = \sum_s n_s s R_s^2 \sim \sum_s n_s s s^{2/d_f};$$

Using Eq. (13.22) for the moments of n_s, as well as (13.21) and (13.28), we find:

$$R_\infty^2 \propto |p - p_c|^{\beta - 2\nu}, \quad p < p_c. \tag{14.8}$$

We thus find an explicit form of the *saturation value* of the MSD in the random walk of the ant in the labyrinth. On the other hand, for $p > p_c$ and $R(t) \to \infty$, we find *an anomalous (but not strange!) diffusive law* of the form (14.3) with a p-dependent diffusion coefficient:

$$R^2(t) \sim \mathcal{D}(p)\, t, \quad p > p_c, \quad R(t) \to \infty \tag{14.9}$$

It was shown in the previous section that, because of the Einstein relation (11.69), the diffusion coefficient has the same p-dependence as the electrical conductivity, i.e., Eq. (14.2), with a dynamical critical exponent μ. All these results can be combined by assuming a *dynamical scaling law* for the MSD:

$$R^2(t) \propto t^{\alpha_c} \rho \left[|p - p_c|\, t^x \right] \tag{14.10}$$

The exponents α_c, x are determined by two conditions. For $z \to \infty$, $\rho(z) \to z^a$, which must be consistent with (14.9); for $z \to -\infty$, $\rho(z) \to z^b$, which must be consistent with (14.8). These constraints yield:

$$t^{\alpha_c} |p - p_c|^a t^{xa} \propto |p - p_c|^\mu t,$$
$$t^{\alpha_c} |p - p_c|^b t^{xb} \propto |p - p_c|^{\beta - 2\nu}.$$

Comparing the exponents on the two sides, we determine a, b, α_c, x; in particular, the exponents in the scaling relation (14.10) are:

$$x = \frac{1}{\mu + 2\nu - \beta}, \tag{14.11}$$

$$\alpha_c = \frac{2\nu - \beta}{\mu + 2\nu - \beta}. \tag{14.12}$$

These equations introduce some important concepts. We first note that for $p = p_c$, the function $\rho(z)$ takes a constant, non-zero value $\rho(0)$, hence:

$$R^2(t) \propto t^{\alpha_c}, \quad p = p_c. \tag{14.13}$$

Thus, α_c is precisely the *diffusion exponent* at the percolation threshold. Given that $\mu > 0$, it follows from (14.12) that $\alpha_c < 1$, hence at the percolation threshold, we have an asymptotic *subdiffusive behaviour* (thus confirming our previous qualitative statement).

The exponent x defines a *cross-over time* t_c which separates the regimes of strange diffusion and anomalous diffusion (for $p > p_c$):

$$
\begin{aligned}
1 &\ll t \ll (p - p_c)^{-1/x}: && \text{strange diffusion} \\
t &\gg (p - p_c)^{-1/x}: && \text{anomalous diffusion}
\end{aligned}
\tag{14.14}
$$

Using Eqs. (13.4), (13.6), (14.2), (14.11), we find:

$$t_c \propto (p - p_c)^{-1/x} = (p - p_c)^{\beta - \mu - 2\nu} \propto P \frac{\xi^2}{\mathcal{D}}. \tag{14.15}$$

This relation implies:

$$\mathcal{D}t_c \approx R^2(t_c) \propto P \xi^2 \tag{14.16}$$

This is not the intuitive Eq. (14.6): there appears an additional factor P. This difference is explained as follows. In the random walk considered here, there is a fraction of ants that remain trapped in the finite clusters as $t \to \infty$; only the ants that started on the infinite cluster at time $t = 0$ contribute to a growing MSD. One could define a *different* random walk problem by considering that the ant starts *certainly* at $t = 0$ anywhere *on the infinite cluster*. This problem yields, for $p > p_c$ and for $t \to \infty$, an anomalous (but not strange) diffusive behaviour: $R^2(t) = 2d\mathcal{D}'t$, with $\mathcal{D}' \neq \mathcal{D}$. For this random walk restricted to the infinite cluster, the cross-over time is indeed provided by Eq. (14.6).

14.3 Strange Diffusion on the Infinite Cluster

We now discuss in some detail the laws governing the diffusion, i.e., *the random walks on a fractal substrate*. The typical case of interest will be the diffusion on the infinite

cluster *at the percolation threshold* $p = p_c$. As was shown above, this process behaves *subdiffusively* in the asymptotic limit $t \to \infty$. We derive an equation of evolution for this process (following the work of O'Shaughnessy and Procaccia [OSP]).

We try to generalize reasonably the ordinary diffusion equation, which we encountered many times in previous chapters:

$$\partial_t n(\mathbf{x}, t) = D \nabla^2 n(\mathbf{x}, t), \tag{14.17}$$

where $n(\mathbf{x}, t)$ is the density profile in a d-dimensional Euclidian space. We consider a system with spherical symmetry, i.e., we suppose that the density profile only depends on the distance over the angles. Writing the Laplacian in (hyper-)spherical coordinates and integrating over the angles, we obtain:

$$\partial_t n(r, t) = \frac{D}{r^{d-1}} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r} n(r, t). \tag{14.18}$$

We denote the probability of finding a particle in a (hyper-)spherical shell between r and $r + dr$ by $m(r, t)\, dr$ and note:

$$m(r, t) = a r^{d-1} n(r, t); \tag{14.19}$$

[for instance, for $d = 3$, $m(r, t) = 4\pi r^2 n(r, t)$]. We thus find:

$$\partial_t m(r, t) = \partial_t r^{d-1} n(r, t) = -\frac{\partial}{\partial r} \left[-r^{d-1} D \frac{\partial}{\partial r} n(r, t) \right]. \tag{14.20}$$

We may look at these equations in two equivalent ways. The basic way is to recognize in (14.18) the continuity equation, combined with Fick's law, and expressed in spherical coordinates:

$$\partial_t n = -\nabla \cdot \boldsymbol{\Gamma}, \quad \boldsymbol{\Gamma} = -D \nabla n; \tag{14.21}$$

the expression of the divergence operator $\nabla \cdot$ introduces the geometrical factor r^{d-1}.

An alternative interpretation consists of looking at (14.20) formally as a continuity equation *in one dimension*, combined with a "Fick-like" law for an "effective one-dimensional particle flux":

$$\partial_t m = -\frac{\partial}{\partial r} \widehat{\Gamma}, \quad \widehat{\Gamma}(r, t) = -r^{d-1} D \frac{\partial}{\partial r} n(r, t) \tag{14.22}$$

The second equation can, in turn, be interpreted as a Fick law with a distance-dependent diffusion coefficient:

$$\widehat{D}(r) = r^{d-1} D \tag{14.23}$$

The "effective diffusion coefficient" $\widehat{D}(r)$ is thus a function growing monotonically like $r^{d_f - 1}$. This second interpretation looks unnatural; it will, however, provide us with a very reasonable generalization from Euclidean to fractal geometry. This generalization requires a *redefinition of the concepts* and *three assumptions*.

Consider a random walk on a fractal support (i.e., the walk of the ant in the labyrinth) rather than on a regular lattice in d dimensions. The argument given here is rather general, and applies to regular fractals (i.e., exactly self-similar structures such as the Sierpinsky gasket, a favourite model of workers in this field because it can be treated analytically) as well as to statistical fractals, such as the *infinite cluster at the percolation threshold*, where $\xi = \infty$. The latter problem will be of special interest to us here. We first note that the probability of finding a particle in r at time t on a fractal background would be an extremely irregular function. In order to obtain a useful formulation we thus identify the density profile $n(r, t)$ with the *smooth envelope* of this function: we thus always work with smooth functions. We now introduce the three assumptions.

A) The probability density $m(r, t)$ for finding a particle in a spherical shell will be factorized as $m(r, t) = n(r, t)\, N(r)$, where $n(r, t)$ is the (smoothed) probability of finding the particle at (r, t) *per site of the fractal*, and $N(r)$ is the number of occupied fractal sites in the spherical layer, per unit of width. Recalling Eq. (13.26), we note that the number of occupied sites, i.e., the mass contained in a sphere of radius r is $\sim r^{d_f}$, we have $N(r) \propto a_f\, r^{d_f - 1}$, hence:

$$m(r, t) = a_f\, r^{d_f - 1}\, n(r, t). \qquad (14.24)$$

This equation generalizes Eq. (14.19).

B) We generalize in a similar way the definition of the "effective diffusion coefficient" 14.23, replacing the Euclidian dimensionality by the fractal one:

$$\widehat{D}(r) = r^{d_f - 1}\, \overline{D}(r). \qquad (14.25)$$

C) In the Euclidian case (14.23) $\overline{D}(r)$ is a constant. In the fractal case, it is not granted that the effective diffusion coefficient grows proportionally to the mass of the shell. We must allow for a possibly slower growth by introducing a distance-dependent diffusivity on the fractal $\overline{D}(r)$ with an additional positive exponent θ (which will be determined later):

$$\overline{D}(r) = r^{-\theta}\, K, \qquad (14.26)$$

where K is now a truly constant coefficient.[5] This additional space dependence reflects the existence of holes on all length scales in the fractal, which explains why

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[5] We do not use the notation D, because the "generalized diffusion coefficient" K has the dimension (length)$^{2+\theta}$/(time), different from the usual diffusion coefficient.

this function grows more slowly than the mass. The (smoothed) effective particle flux is now obtained from Eq. (14.22):

$$\hat{\Gamma}(r,t) = -r^{d_f-1-\theta} K \frac{\partial}{\partial r} n(r,t). \tag{14.27}$$

We now collect the results (14.24) - (14.28) and substitute them into the continuity equation (14.22):

$$\partial_t n(r,t) = \frac{K}{r^{d_f-1}} \frac{\partial}{\partial r} r^{d_f-1-\theta} \frac{\partial}{\partial r} n(r,t). \tag{14.28}$$

This is the *generalized diffusion equation* derived by O'Shaughnessy and Procaccia in 1985. It describes the diffusive process on a fractal. Its authors have also derived its fundamental solution (propagator), properly normalized to 1, which reduces to $\delta(r)$ at time $t = 0$; this solution is easily checked by direct substitution:

$$n(r,t) = \frac{2+\theta}{\Gamma\left(\frac{d_f}{2+\theta}\right)} \left[\frac{1}{K(2+\theta)^2 t}\right]^{d_f/(2+\theta)} \exp\left[-\frac{r^{2+\theta}}{K(2+\theta)^2 t}\right]. \tag{14.29}$$

This function is very similar to the Gaussian profile (12.26) [for $V = 0$] obtained for the ordinary random walk in Euclidean space. Eq. (14.29) reduces to the latter when $d_f = d$ and $\theta = 0$. This solution is plotted in Fig. 14.4a as a function of the similarity variable $q = r/t^{1/(2+\theta)}$ for three different times ($Kt = 1, 4, 10$) and compared (Fig. 14.4b) to the diffusive profile (for which $d_f = d = 2$, $\theta = 0$)[6]: it shows qualitatively the usual spatial dispersion.
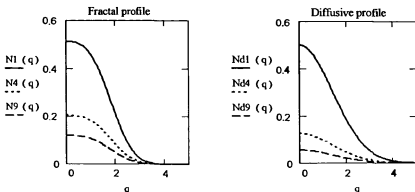

Figure 14.4. Density profiles vs. similarity variable

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[6]The values of the exponents in these graphs are determined from the forthcoming relations.

A comparison with the diffusive solution ($d_f = d = 2$, $\theta = 0$) is very instructive (Fig. 14.5). It shows that the fractal profile remains, at all times, more concentrated near the origin and has therefore a shorter tail than the Gaussian profile.
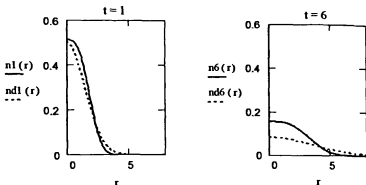

Figure 14.5. Density profiles vs. position. Solid: fractal, dotted: diffusive.

The first obvious remark is that Eq. (14.29) is a *scaling relation*, just like the Gaussian law (12.26) or the CTRW profile (12.64):

$$n(r,t) \propto t^{-d_s/2} F(\frac{r^{d_w}}{t}). \tag{14.30}$$

This scaling form could have been (and has been) conjectured independently of the generalized diffusion equation (14.28). The solution of the latter provides us with an explicit form of the function F, but many results can be derived without the knowledge of this form. In particular, the time dependence of the moments is obtained as follows:

$$\langle r^{2q}(t) \rangle = \frac{\int dr\, r^{d-1} r^{2q} t^{-d_s/2} F(\frac{r^{d_w}}{t})}{\int dr\, r^{d-1} t^{-d_s/2} F(\frac{r^{d_w}}{t})} = \frac{\int dz\, t^{2q/d_w} z^{(d-d_w+2q)/d_w} F(z)}{\int dz\, z^{(d-d_w)/d_w} F(z)}$$

thus:

$$\langle r^{2q}(t) \rangle = C_q\, t^{(2/d_w)q}, \tag{14.31}$$

with:

$$C_q = \frac{\Gamma\left(\dfrac{d_f + 2q}{2 + \theta}\right)}{\Gamma\left(\dfrac{d_f}{2 + \theta}\right)} \left[(2 + \theta)^2 \, K\right]^{(2/d_w)q}. \tag{14.32}$$

This result confirms our previous result (14.13): this system exhibits a *subdiffusive behaviour*. We now see that *the exponent d_w is directly related to the diffusion exponent for the random walk on the infinite cluster*:

$$\langle r^2(t) \rangle = C_2 \, t^{\overline{\alpha}}, \qquad \overline{\alpha} = \frac{2}{d_w} = \frac{2}{2 + \theta}. \tag{14.33}$$

It is readily checked that in the Euclidean case, $d_f = d$, $\theta = 0$, Eqs. (14.31), (14.32) reduce to those obtained for the Gaussian profile, (12.87), (12.90). The MSD given by Eq. (14.33) is plotted in Fig. 14.6 and compared to the Euclidean, diffusive law for $d = 2$.[7] It is striking that the subdiffusive curve deviates very strongly from the diffusive one, even for short times ($Kt \approx 10$).
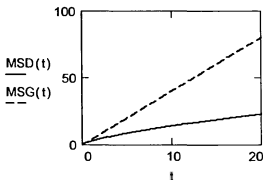
Figure 14.6. Mean square displacement. Solid: subdiffusive, Dashed: Gaussian.

We now interpret the exponent d_s appearing in Eq. (14.30). Consider first the Gaussian profile (12.26) with $V = 0$. The probability to return to the origin after a time t is obtained by setting $r = 0$ in that equation:

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[7] The value of the exponent θ is given by the forthcoming formula (14.36), with numerical values taken from Table 13.1. For $d = 2$ one finds: $\theta = 0.871$ and $\overline{\alpha} = 0.697$.

$$n(0,t) = (2\pi Dt)^{-d/2} \propto R(t)^{-d}. \tag{14.34}$$

This quantity is thus inversely proportional to the volume, or the mass of the region visited by the ant in a time t.

Eq. (14.29) allows the same interpretation; but now the mass of a region of linear size $R(t)$ scales as $R(t)^{d_f}$, because the ant is restricted to move on the fractal. Combining this with (14.33), we obtain:

$$n(0,t) \propto R(t)^{-d_f} \propto t^{-(d_f/d_w)},$$

thus, comparing with (14.30):

$$d_s = \frac{2d_f}{d_w}. \tag{14.35}$$

The parameter d_s is called *fracton dimension* (or spectral dimension).

We now show that the newly introduced exponents are related to the basic ones. Consider a random walk on the infinite cluster for $p = p_c + \varepsilon$ (in order to have a finite correlation length ξ). We write the Einstein equation relating the conductivity $\Sigma(|p - p_c|)$ to the diffusion coefficient. The latter is expressed as the diffusivity $\overline{D}(r)$ for an ant on the infinite cluster, times the probability $P(|p - p_c|)$ of belonging to that fractal cluster:

$$\boxed{G \sim \Sigma(|p - p_c|) \propto \overline{D}(r)\, P(|p - p_c|).}$$

Using Eqs. (14.1), (14.26) and (13.4), this implies:

$$|p - p_c|^{\mu} \propto K r^{-\theta} |p - p_c|^{\beta}.$$

This can be re-expressed in terms of $\xi \propto |p - p_c|^{-\nu}$:

$$\xi^{-\mu/\nu} \propto K r^{-\theta} \xi^{-\beta/\nu}.$$

This equation is valid, in particular, for $r = \xi$. We then find the relation:

$$\theta = \frac{\mu - \beta}{\nu}. \tag{14.36}$$

This is the relation we were looking after: it connects the exponent θ, hence also d_w, d_s to the three basic exponents β, ν, μ. Combining Eqs. (14.33) and (14.36) we find:

$$\overline{\alpha} = \frac{2\nu}{2\nu + \mu - \beta}. \tag{14.37}$$

It is noteworthy that this result differs from the exponent α_c obtained in Eq. (14.12). This is due to the different definitions of the random walk in the two cases. Here the ant is restricted to the infinite cluster whereas in the previous case it could explore the whole lattice. As mentioned at the end of Sec.14.2, this leads to different values of the diffusion exponent; it is therefore not surprising that the difference is related to β, hence to the probability of belonging to the infinite cluster.

Let us finally comment on the relation between the fracton dimension and the basic exponents. Using Eqs. (14.33), (14.35), (14.36) as well as (13.30) we find:

$$d_s = \frac{2d_f}{d_w} = 2\frac{d\nu - \beta}{2\nu + \mu - \beta}. \tag{14.38}$$

This relation led to some excitement, because it was shown that $d_s = \frac{4}{3}$ exactly for $d \geq 6$ (in particular, for the Bethe lattice), whereas numerical simulations led Alexander and Orbach (1982) to the conjecture:

$$\boxed{d_s = \frac{4}{3}, \quad \forall d \geq 2} \quad \text{(A-O conjecture)}. \tag{14.39}$$

If this conjecture were exact, it would lead to the important conclusion that the non-equilibrium conductivity exponent μ could be related to the two basic static exponents β and ν. Unfortunately, this conjecture was disproved by more accurate simulations and by renormalization group arguments. It remains, nevertheless, an excellent approximation (for instance, for $d = 2$, very accurate simulations yield $d_s = 1.32$ instead of 1.33...).

14.4 Conclusions

The results of the present chapter attract our attention on two important features of transport theory.

- The transport laws in disordered systems can be very different from those of classical, collisional transport theory, presented in Chap. 10. Far from the critical point, there exist finite transport coefficients, which depend on the degree of disorder. This situation corresponds to ANOMALOUS TRANSPORT.

- The transport laws are deeply modified in the *critical region*. The diffusive laws are no longer valid: they are replaced by a *subdiffusive behaviour*, hence a regime of STRANGE TRANSPORT.

There is still much work to be done in developing this fascinating field, which has applications in very numerous fields of physics.

14.5 Bibliographical Notes BN14

An extensive review of dynamical (thermal) critical phenomena is found in:

Hohenberg, P.C. and Halperin, B.I., 1977, Rev. Mod. Phys., **49**, 435.

A recent review of the *electrical conductivity* in disordered materials is:

Clerc, J.P., Giraud, G., Laugier, J.M. and Luck, J.M., 1990, Adv. Phys., **39**, 191.

The basic experiment on electrical conductivity is:

Last, B.J. and Thouless, D.J., 1971, Phys. Rev. Lett., **27**, 1719.

The problems connected with *diffusion in disordered media* is extensively reviewed in the following works, where many additional references will be found:

Havlin, S. and Ben Avraham, D., 1987, Adv. Phys., **36**, 695,
Bouchaud, J.Ph. and Georges, A., 1990 (**BN13**),
Stauffer, D. and Aharony, A., 1992 (**BN13**).

The celebrated *"ant in labyrinth"* model was introduced in:

de Gennes, P.G., 1976 (**BN13**).

The problems of *anomalous and strange diffusion* are discussed in:

Ben Avraham, D. and Havlin, S., 1982, J. Phys., A **18**, L691,
Gefen, Y., Aharony, A. and Alexander, S., 1983, Phys. Rev. Lett., **50**, 77,
Mitescu, C.D. and Roussenq, J., 1983, in: *Percolation Structures and Processes* (**BN13**),
O'Shaughnessy, B. and Procaccia, I., 1985, Phys. Rev., A **32**, 3073,
Harris, A.B., Meir, Y. and Aharony, A., 1987, Phys. Rev. B **36**, 8752.

Some very interesting applications of percolation theory to diffusion in turbulent plasmas (and other anomalous diffusion problems) are based on the ideas that the magnetic field lines obey equations of Hamiltonian structure. The field lines thus move on surfaces of constant "energy", thus trying to find their way through a mountainous landscape. When the magnetic field is stochastic, the landscape becomes very rugged (in each realization) and the field lines become very tortuous, and possibly fractal. Anomalous diffusion is thus related to a problem of *statistical topography*. We have no space for an exposition of this approach, which is developed in:

Kadomtsev, B.B. and Pogutse, O.P., 1979, in: *Plasma Physics and Controlled Nuclear Fusion Research*, Proc. 7-th Int. Conf. Innsbruck, 1978, vol. 1, Int. Atomic Energy Agency, Vienna, p. 649,
Gruzinov, A.V., Isichenko, M.B. and Kalda, Ya.L., 1990, Sov. Phys. JETP, **70**, 263,
Isichenko, M.B. and Kalda, Ya.L., 1991, J. Nonlinear Sci., **1**, 375,
Isichenko, M.B., 1991, Plasma Phys. Contr. Fusion, **33**, 809.

An extensive review of this type of works is given in:

Isichenko, M.B., 1992, Rev. Mod. Phys., **64**, 961.

These works benefitted from an important exact mathematical result on the fractal dimension of the *hull of percolation clusters*:

Saleur, H. and Duplantier, B., 1987, Phys. Rev. Lett., **58**, 2325.

Chapter 15

Chaos and Transport

15.1 The Standard Map

In Chap. 14 we studied transport processes occuring in disordered systems, modelled as percolative structures. In those problems the type of disorder is prescribed. We now consider systems where *the disorder is created by the dynamics itself*. One of the great advances of the second half of this century was the discovery that systems governed by perfectly deterministic laws of motion may behave in such a complex way as to simulate a random motion. This phenomenon of DETERMINISTIC CHAOS has been intensely studied and has found many applications. We can only briefly discuss here a few aspects that are related to the problem of transport and to statistical dynamics.

In principle, the study of the evolution of a material system should start from the equations of motion. It is well known that Hamiltonian systems generally are subject to extremely complex motions. Hamilton's equations for systems of more than one degree of freedom are generically non-integrable. Even their numerical study poses serious problems and requires very precise algorithms and a very fine discretization of the time (hence very long computing times) in order to be sure that the results are significant (rather than due to accumulations of numerical errors). For this reason, the study of these systems is very often replaced by a reduced (hence incomplete) description, which has the advantage of greater simplicity.

Consider a conservative *Hamiltonian system with two degrees of freedom*: its phase space is 4-dimensional. (The procedure can be generalized to higher dimensions, but we shall only discuss this important special case). The energy being conserved, the motion occurs along an orbit lying on the three-dimensional energy hypersurface. If the orbits are bounded, we may consider a two-dimensional *surface of section (or Poincaré surface of section)*, for instance, by fixing one of the coordinates. As time passes, the orbit will repeatedly cross this surface. The successive intersection

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points are recorded: their sequence constitutes a discrete "orbit", which contains very valuable information about the motion. The iterates obtained by this procedure are labelled by an index ν, which plays the role of "time". Note that successive points of the map are interrelated by a canonical transformation in the complete phase space. The resulting law connecting any point of this sequence to its predecessor is called a MAP.

A concrete example of a system conforming to this description is provided by the magnetic field lines in a tokamak. It is known that in this device a plasma is confined by a magnetic field with a toroidal configuration. In a simplified and ideal picture, the field lines are all tangent to magnetic surfaces, which are nested circular tori, as shown in Fig. 15.1. Using toroidal coordinates as shown in the figure, i.e., a radial coordinate r, a poloidal angle θ and a toroidal angle ζ, the magnetic surfaces are the tori $r = const$. The toroidal coordinate can be considered as a parameter playing the role of "time": the field lines are curves defined by differential equations of the form $d\mathbf{B}/d\zeta = \mathbf{F}(r, \theta, \zeta)$. They have a Hamiltonian structure (because of the property $\nabla \cdot \mathbf{B} = 0$).
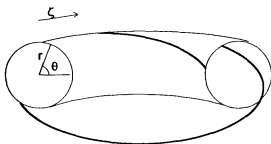

Figure 15.1. A magnetic field line in a tokamak.

Instead of solving these complicated equations, one may introduce a Poincaré surface of section: $\zeta = 0$, and record the successive crossing points of the field line with this plane (Fig. 15.1). A field line starting at $\zeta = 0$ turns around the torus in the toroidal direction and simultaneously coils up in the poloidal direction. After a complete tour in ζ, the line hits the Poincaré surface at a point that differs (in general) from the starting point. In the ideal case described above, the successive intersections are aligned on a circle. When a perturbation (fluctuation, irregularity

in the field,...) is introduced, the magnetic surfaces may be destroyed. In that case, the magnetic field lines fill a three-dimensional region; hence their images in the map fill a two-dimensional domain. This is the phenomenon of *field line "diffusion"*, which is of considerable importance for the feasibility of fusion.

Let $\mathbf{X}_\nu = (X_{1,\nu}, X_{2,\nu})$ denote the set of values of the coordinates at "time" ν ($\nu = 0, \pm 1, \pm 2, \ldots$): this ordered set will be called an ORBIT for the map. The map is defined by an *equation of evolution* by which the values of the coordinates at a given "time" $\nu + 1$ are determined as functions of their values at the previous "time"; the map generally depends on a control parameter K (or, possibly, on several such parameters). We thus write:

$$\mathbf{X}_{\nu+1} = T_K(\mathbf{X}_\nu). \tag{15.1}$$

All maps derived from a Hamiltonian have the property of *area-preservation* in the *phase space*, i.e., (in the present context) the space defined by the two relevant coordinates. We assume that one of these coordinates is an *angle*, denoted by $2\pi\theta$, the other coordinate will be denoted by x. The map is thus defined by:

$$\begin{aligned}
x_{\nu+1} &= R_K(x_\nu, \theta_\nu), \\
\theta_{\nu+1} &= \Theta_K(x_\nu, \theta_\nu).
\end{aligned} \tag{15.2}$$

Both R_K and Θ_K are periodic functions of θ, with period 1. The phase space has thus a cylindrical structure: the motion of the phase point is restricted to a cylinder of arbitrary radius, and infinite length in both directions. The representation is clearer if this cylinder is unfolded into a rectangular strip. We must assume periodic boundary conditions in the θ-direction. We shall most often study the motion in a limited range of x, e.g. $[0, 1]$ or $[-\frac{1}{2}, \frac{1}{2}]$.

Our study will be devoted to a more limited class of area-preserving maps. We first define the class of TWIST MAPS as follows:

$$\begin{aligned}
x_{\nu+1} &= x_\nu + K f(\theta_\nu), \\
\theta_{\nu+1} &= \theta_\nu + g(x_{\nu+1}) \pmod 1.
\end{aligned} \tag{15.3}$$

Here $f(\theta)$ is a periodic function of θ: $f(\theta + 1) = f(\theta)$; the function $g(x)$ satisfies the so-called *twist condition*:

$$\frac{dg(x)}{dx} \neq 0, \quad \forall x. \tag{15.4}$$

K is a real, non-negative number: it is called the *Stochasticity parameter*. In the second equation, $x_{\nu+1}$ is to be understood as the right hand side of the first equation: it is thus a function of (x_ν, θ_ν).

Most of our discussions will refer to a special twist map defined as follows:

$$x_{\nu+1} = x_\nu - \frac{K}{2\pi} \sin 2\pi\theta_\nu,$$
$$\theta_{\nu+1} = \theta_\nu + x_{\nu+1} \pmod{1}. \tag{15.5}$$

Eq. (15.5) defines the so-called STANDARD MAP, introduced by *Chirikov* in 1979 and studied in a vast amount of works. In this case, $f(\theta) = -\frac{K}{2\pi} \sin 2\pi\nu$, and we have the simple relation: $g(x) = x$. The study of the standard map provides us with a concrete illustration of the generic properties of two-dimensional area preserving maps (some properties are, however, specific to this map: these will be explicitly identified below).

We now introduce a classification of the various orbits in a twist map. If we plot the successive values of $\mathbf{X}_\nu$, on the phase space graph, there appear orbits having very different topological properties, according to the initial condition and to the value of the stochasticity parameter:

• **1) CYCLES:** These correspond to PERIODIC ORBITS of period q. They are easily identified on the graph as *a set of q discrete points*. Starting the iteration at one of them, the representative point jumps from one of the points to the other and returns at the q-th step to its initial position, after which the process repeats periodically [1]. Thus:

$$\mathbf{X}_{\nu+q} = \mathbf{X}_\nu. \tag{15.6}$$

• **2) INVARIANT KAM CURVES:** The sequence never repeats, i.e., the point never returns to its initial position, but the successive points *densely fill a curve* Γ. (The existence of such curves was discovered by Kolmogorov, and led to the celebrated Kolmogorov - Arnold - Moser theorem, whence the name "KAM".) More formally, these orbits are defined as follows: For every point $\mathbf{x} \in \Gamma$, one can find a subsequence $\mathbf{X}_{\nu_s}$ of $\mathbf{X}_\nu$ such that $\lim_{s\to\infty} \mathbf{X}_{\nu_s} = \mathbf{x}$. The invariant KAM curves can be further subdivided into two classes:

---

[1] The standard map (but not the general twist map (15.3) has the property that x is also an angular variable, like θ; indeed, from (15.5) follows that $x_{\nu+1} = \theta_{\nu+1} - \theta_\nu$. As a result, there exists a special class of generalized cycles ("period-q, step-l cycles") defined by:

$$x_{\nu+q} = x_\nu + l = x_\nu \pmod{1}, \quad \theta_{\nu+q} = \theta_\nu + p = \theta_\nu \pmod{1}.$$

Instead of being a fixed point, such an orbit advances in the x-direction (by l units) upon every q-th iteration. These cycles are adequately called "accelerator modes". Analysis shows that they exist and are stable only in certain windows of K. Thus, the region of stability for $q = 1$ modes is: $2\pi l < K < 2\pi l \left[1 + (2/\pi l)^2\right]^{1/2}$. Note that all these values are supercritical: $K > K_c$ (see below). Accelerator modes produce a special kind of strange transport briefly mentioned at the end of Sec. 15.4.

- **2a) Trapped orbits:** These are CLOSED CURVES around each of the q points of a periodic cycle. The successive representative points jump from one component of the (disconnected) curve to another. The trapped orbits are organized concentrically around the points of the periodic cycle in a region of finite width called an **ISLAND CHAIN**. Clearly, an island chain around a q-cycle consists of q individual islands. The edge of an island chain is *not* a smooth curve; rather, a *secondary island chain* is formed, which encircles the primary islands. Around each secondary island there appears a third-order island chain, and so on. We thus see a typical *self-similar structure* developing at the edge of each island chain.

- **2b) Passing orbits:** These are orbits encircling the cylinder, or else, spanning the whole width of the rectangle representing the phase space from $\theta = 0$ to $\theta = 1$. These will be called **KAM BARRIERS** for reasons that will be presently clear.

- **3) CHAOTIC ORBITS:** Here again, the sequence never repeats, but the successive points *densely fill a* TWO-DIMENSIONAL REGION R_c. Thus, for every point $\mathbf{x} \in R_c$, there exists a subsequence $\mathbf{X}_{\nu_s}$ of $\mathbf{X}_\nu$ such that $\lim_{s \to \infty} \mathbf{X}_{\nu_s} = \mathbf{x}$.

All these orbits are illustrated in Fig. 15.2 for the standard map with $K = 0.8$.
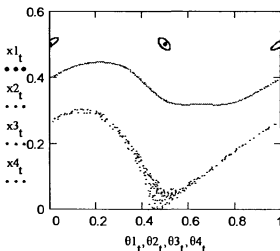

Figure 15.2. Cycle, Island Chain, KAM barrier and chaotic orbit.

Consider now a region $\mathcal{R}$ bounded by two passing KAM orbits. It can be shown that all the iterates of an arbitrary point of that region are contained in $\mathcal{R}$:

$$\forall X \in \mathcal{R}: \quad T_K^\nu(X) \in \mathcal{R}.$$

In particular, *a chaotic orbit contained in* $\mathcal{R}$ *cannot ever cross the limiting KAM curves.* It is for this reason that the passing orbits are called KAM barriers.

Consider now what happens with a twist map (15.3) when the stochasticity parameter K varies.

When $K = 0$, the orbits are easily found analytically (the map is *integrable*):

$$x_{\nu+1} = x_\nu, \qquad \theta_{\nu+1} = \theta_\nu + g(x_\nu) \pmod 1. \qquad (15.7)$$

The solution of these equations is trivial. If (x_0, θ_0) is the initial condition, the coordinates at arbitrary time ν are:

$$x_\nu = x_0, \qquad \theta_\nu = \theta_0 + \nu g(x_0) \pmod 1. \qquad (15.8)$$

All orbits have a constant x, hence they are aligned along horizontal lines in the phase space plot. We may also define the "lift" as the full value of the angle $\theta_\nu^* = \theta_0 + \nu g(x_0)$, counted without the restriction (mod 1).

We now introduce an important concept associated with every periodic cycle and with every KAM curve. The WINDING NUMBER (or *rotation number*) is defined as follows for an orbit starting initially at (x_0, θ_0):

$$W(x_0) = \lim_{\nu \to \infty} \frac{\theta_\nu^* - \theta_0}{\nu}. \qquad (15.9)$$

The winding number depends on the initial value of the radial coordinate x_0.[2] For the *unperturbed* twist map under discussion ($K = 0$), the winding number is easily found from (15.8):

$$W(x) = g(x), \qquad (\text{twist map, } K = 0). \qquad (15.10)$$

In particular, for the unperturbed standard map, we have:

$$W(x) = x, \qquad (\text{standard map, } K = 0). \qquad (15.11)$$

The winding number allows us to characterize the two types of orbits existing in the unperturbed twist maps. Whenever we reach a value of x for which the winding number has a *rational value*:

$$W(x) = \frac{p}{q}, \qquad (15.12)$$

---

[2] It can be shown that the winding number is independent of the initial value of the angle.

(where p, q are positive integers without any common factor) the orbit (15.8) has a special behaviour. Starting from any value of ν, we find after q iterations:

$$
\begin{aligned}
x_{\nu+q} &= x_\nu = x_0, \\
\theta_{\nu+q} &= \theta_\nu + q \cdot \frac{p}{q} = \theta_\nu + p = \theta_\nu \pmod 1.
\end{aligned}
\qquad (15.13)
$$

Thus, whenever $W(x_0)$ is a *rational* number the phase point eventually returns to its initial value: the orbit is a *cycle*. On the contrary, when $W(x_0)$ is *irrational*, the point never returns to its starting position, and the orbit densely fills a horizontal line: it is a *KAM barrier*. We also note that the property (15.13) is true for all values of θ_ν. Thus, *any point on the straight line* $W(x) = (p/q)$ *is a fixed point (cycle) of period* q.

We now consider the *perturbed twist maps*, $K \neq 0$. In this case, many of the properties described above are lost. We note first that we may still define a *winding number* $W(x_0)$ by Eq. (15.9), but the identifications (15.10), (15.11) are no longer valid. We now quote (without proof) a beautiful and simple theorem. We start with the unperturbed twist map and consider the rational curve with $W(x) = (p/q)$: all its points are fixed points. We now perturb the map by introducing a small term for $K \neq 0$.

The Poincaré-Birkhoff theorem then states that *there remains an even number* $2mq$ *of fixed points of period* q *on this curve*. (Here m is some positive integer that is not determined by the theorem; most often $m = 1$ to which we restrict ourselves below).

The $2q$ fixed points on a rational curve are of two types: there are exactly q *elliptic points* (or stable, or O-points) and q *hyperbolic points* (or unstable, or X-points) located in between the elliptic ones. Under repeated iterations, a point near an elliptic fixed point will circle around it; a point near a hyperbolic fixed point is driven away from it by the map. We thus see that the topology of the phase space is deeply changed by the perturbation. Near every rational surface with winding number $W = p/q$ there appear closed regular orbits encircling the q elliptic points, forming a *chain of* q *islands*. The motion near a hyperbolic point is much more complicated: it is in this neighbourhood that a *chaotic layer* starts. Nevertheless, for sufficiently small K (i.e., before the development of global chaos), the alternation of O-points and X-points is a generic property of the system. Thus, instead of only two types of orbits (cycles and KAM barriers), all the types listed above will appear as K increases.

A most important fact concerns the KAM barriers, which gradually "disappear". This happens as follows. Consider a given barrier. As K increases, it reaches a value where the KAM curve changes its character. Instead of a continuous curve it develops holes which transform it into a *fractal*, analogous to a Cantor set. Such a structure is

adequately called a CANTORUS. These holes are possible "exit points" for a chaotic orbit which was formerly blocked by the KAM barrier: the cantori are "permeable". As K continues to grow, the "holes" become larger, until any observable trace of the initial barrier has disappeared.[3]

The various KAM barriers do not disappear at the same K: some are more robust than others. The chaotic regions occupy more and more area in the phase space, until a final critical value K_c is reached, when the last KAM barrier is destroyed. After this, the chaotic orbits can extend indefinitely in the x direction: there are no more any barriers and one speaks of *global chaos*. There still remain, however, regions bounded by *islands*, which remain inaccessible to the chaotic orbits; these regions are shrinking as K increases, and as $K \to \infty$, all islands disappear and the whole phase space is covered by chaotic orbits.[4] These various situations are illustrated in Fig. 15.3. In the first situation $K = 0.97$: this is very close to, but below the critical stochasticity parameter. The orbit represented there starts at $x_0 = 0.61$, $\theta_0 = 0.45$, i.e., very close to the golden KAM barrier (see below). This is a chaotic orbit, that remains confined below this barrier, in a region around an island chain. In the second picture, $K = 2.5$ and the unique orbit represented there starts at the same initial condition as the first. The orbit is completely different: all barriers are broken, and the orbit extends over the whole range of x. We showed here the range $0 < x < 3$, but waiting long enough, all values of x, both positive and negative, will be reached. The remaining islands are, however, clearly seen.

As the stochasticity parameter K grows, the rational curves are immediately destroyed and replaced by island chains. The irrational curves are more robust: most of them subsist in the perturbed map as KAM barriers; however, they will also progressively be destroyed (they become cantori) as K increases. An important question is: which KAM barrier is the most robust (i.e. the last one to be destroyed), and what is the critical value K_c for which its destruction happens? This question has been answered for the standard map in a classical paper by GREENE by using a beautiful mix of theoretical (renormalization) and numerical arguments. We cannot go into the detailed exposition of his work here, but rather summarize its main results.

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[3]The description given here is only a very superficial introduction: these processes will be discussed in more and more detail in the forthcoming text.

[4]The evolution described here is qualitatively analogous to the phenomena discussed in Chap. 13. The critical stochasticity parameter K_c is analogous to the percolation threshold p_c. Below K_c the map's orbits are confined to bounded regions ("finite clusters"); for $K > K_c$, the orbits can extend indefinitely in x, like in an infinite percolation cluster; there still remain, however, island chains ("finite clusters") which only disappear when $K \to \infty$ ("$p \to 1$").
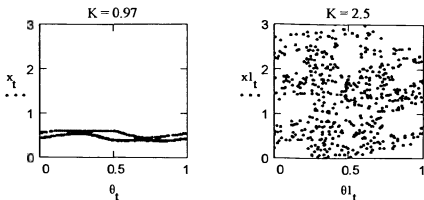
Fig. 15.3. Transition from confinement to global chaos.

Intuitively, one would guess from the previous discussion that the most robust KAM barriers are those which are "the most irrational". The question then arises about the meaning that can be given to these words. The solution given by Greene is based on the following well-known fact. *Any real positive number X can be represented as a continued fraction:*

$$X = x_0 + \cfrac{1}{x_1 + \cfrac{1}{x_2 + \cfrac{1}{x_3 + ...}}} \qquad (15.14)$$

A graphically more convenient notation is: $X = [x_0, x_1, x_2, x_3, ...]$. Here x_j are positive integers. A rational number contains only a finite number J of terms (i.e., $x_k = 0$ for $k > J$); for an irrational number the fraction contains an infinite number of levels. Any irrational number can be approximated by rational numbers (called *convergents*) by truncating the continued fraction at a certain level. Clearly, if the successive x_j are large, the series converges very rapidly, i.e., the number is "very close" to a rational number. It therefore follows that a natural definition of "the most irrational number" [in the range $(0,1)$] is: $w_* = [0, 1, 1, 1, 1, ...]$. This very remarkable number has been celebrated since the ancient Greeks: it is the inverse of the famous GOLDEN SECTION G_*:

$$W_* = \frac{\sqrt{5} - 1}{2} = \frac{1}{G_*} = G_* - 1 \approx 0.618034.... \tag{15.15}$$

The convergents of the golden section are related to another set of celebrated numbers studied in Renaissance times: the FIBONACCI NUMBERS F_n defined as follows:

$$F_1 = F_2 = 1, \quad F_n = F_{n-1} + F_{n-2}. \tag{15.16}$$

The successive convergents of W_* are:

$$C_n = \frac{F_{n-1}}{F_n}. \tag{15.17}$$

Coming back to our problem, Greene has shown (and confirmed numerically) that *the most robust KAM barrier for the standard map is indeed the one whose winding number equals the inverse golden section* W_*. This last barrier is broken when the stochasticity parameter reaches the critical value (determined numerically):

$$K_c = 0.971635... \tag{15.18}$$

For $K > K_c$ we reach the state of global stochasticity, as described above.

15.2   The Perron-Frobenius Operator

In previous chapters we exhibited two complementary methods of studying the evolution of a complex system. One of them is based on *orbits of individual particles* and their complicated dependence on initial conditions (typically: the theory of stochastic processes based on the Langevin equation). Alternatively, one may study the evolution of a *probability distribution function in phase space* (typically: the Liouville equation, or the hybrid kinetic equation): this will yield a more direct link to macroscopic physics.

The object of our study here will be the *density profile* of the system. Instead of considering a single orbit, we now consider an *ensemble* of orbits, each governed by the same standard map, but starting with different initial conditions distributed over the whole phase space. After ν iterations of the map, we average the results over all the initial conditions and determine the *distribution function* of the "particles" in phase space at "time" ν: $f(x, \theta; \nu)$. When this function is integrated over the angular variable θ, it yields the *density profile*: $n(x; \nu)$, i.e., the probability density of finding a particle at the radial position x at time ν.[5] In order to describe the temporal evolution of these objects we need a generalization of the tools used in

---

[5]From now on, we omit the quotation marks for "particles" and "time".

ordinary statistical mechanics. Indeed, we are no longer given an evolution law in *continuous time* that determines the state of the system at every real value of the time, but rather a *map*, determining the state only at *discrete times*: the state of the system in between these times is unknown (it is not an object of the theory).

Let us first recall some of these tools used in ordinary, continuous time statistical mechanics. We consider a dynamical system, whose coordinates define a phase space. Let $F(t)$ be the distribution function: it depends on the phase space coordinates and on time (the former dependence is not written out explicitly here). The evolution of the system (the dynamical law) is defined by a differential equation of the form (3.16):

$$\partial_t F(t) = L F(t) = [H, F(t)],$$ (15.19)

where L is an operator acting in the space of distribution functions. When the dynamics is *Hamiltonian*, L is the *Liouvillian*, defined as the Poisson bracket of the Hamiltonian with the distribution function (3.17). It is important to note that the sign is opposite to the one appearing in the law of motion of the phase space coordinates $\mathbf{X}(t)$, or of any dynamical function (2.14):

$$\dot{\mathbf{X}}(t) = -[H, \mathbf{X}(t)].$$ (15.20)

(Most of the forthcoming considerations apply also to non-Hamiltonian systems; for simplicity, we call the corresponding evolution operator a *Liouvillian*, even if it has to be understood in a generalized sense). The solution of Eq. (15.19) for a given initial condition (and appropriate boundary conditions in the phase space), defines the statistical state of the system for every value of the *continuous time* variable t. Formally, the solution of the initial value problem of Eq. (15.19) [see (3.13)] is written as:

$$F(t) = e^{Lt} F(0).$$ (15.21)

The operator e^{Lt} is the *propagator* relating the solution at time t to the initial state. Because of the different signs in Eqs. (15.19) and (15.20) it is well known that the solution of the Liouville equation (3.18) can be written as follows:

$$F[\mathbf{X}; t] = F[\mathbf{X}(-t); 0].$$ (15.22)

Thus the distribution function in phase-space $\mathbf{X}$ at time t is the same as it was at time 0 at a position traced *backward* in time from point $\mathbf{X}$ along the particle orbit. (This requires, of course, the knowledge of the solution of the equations of motion!).

An important related concept is the *resolvent operator* $R(z)$ defined as the Laplace transform of the propagator:

$$F(t) = \frac{1}{2\pi} \int_{\Gamma} dz \, e^{-izt} R(z) F(0), \qquad (15.23)$$

where Γ is a straight line parallel to the real axis and lying above all the singularities of $R(z)$. Comparing Eqs. (15.21) and (15.23) we find:

$$R(z) = \frac{1}{-iz - L}. \qquad (15.24)$$

The resolvent operator was introduced previously in Chap. 5 for the linearized Vlasov operator, Eqs. (5.46), (5.52).

By introducing an appropriate basis, the operators L and $R(z)$ can be represented as matrices. The eigenvalues of these matrices define the *spectrum* of the corresponding operators; they also determine the type of time dependence of the solution. Obviously, *for any stable dynamical system, the resolvent may have singularities only in the lower complex half-plane or on the real axis* [see Sec. 5.4].

We now consider how these concepts can be generalized to the case of an evolution law described by a *map*, i.e., in *discrete* time. In this case, the statistical state of the system [i.e., the phase space distribution function $f(x, \theta; \nu)$] is only defined at a *sequence of discrete, equidistant times* which, by proper scaling, can always be taken as the sequence of integers: $t = 0, 1, ..., \nu, ...$ Clearly, the differential formulation (15.19) looses its meaning, but the global formulation (15.21) is acceptable for integral values of the time:

$$f(\nu) = e^{L\nu} f(0). \qquad (15.25)$$

This equation has the structure of a ν-fold iteration of an elementary operator U_K which appears to be the exponential of the Liouvillian (this operator depends on the control parameter K). We thus introduce the operator:

$$e^L \Longrightarrow U_K. \qquad (15.26)$$

U_K is called the **PERRON-FROBENIUS operator** associated with the map. The important point is that this operator is well defined even when L looses its meaning, because U_K is not involved in a differential equation. It is thus always meaningful to write Eq. (15.25) in the form:

$$f(\nu) = U_K^{\nu} f(0). \qquad (15.27)$$

Equivalently, one can write the evolution law as:

$$f(\nu) = U_K f(\nu - 1). \qquad (15.28)$$

Clearly, the Perron-Frobenius operator completely defines the action of the map on the distribution function. It plays the same role in the functional space of the

distribution functions as the operator T_K acting on individual phase-space points $\mathbf{X}_\nu$, as defined in Eq. (15.1):

$$\mathbf{X}_\nu = T_K\left(\mathbf{X}_{\nu-1}\right). \qquad (15.29)$$

We now assume that the map T_K is *invertible*, i.e., there exists an *inverse map* T_K^{-1} which determines the evolution towards negative times:

$$\mathbf{X}_{-\nu} = T_K^{-1}\left(\mathbf{X}_{-(\nu-1)}\right). \qquad (15.30)$$

We then find a generalization of Eq. (15.22) in the form:

$$f\left[\mathbf{X};\nu\right] = f\left[\mathbf{X}_{-\nu};0\right] = f\left[T_K^\nu \mathbf{X}; \nu-1\right]. \qquad (15.31)$$

We now consider the resolvent operator. We could try to define it by Eq. (15.23) for integer values of t:

$$f(\nu) \stackrel{?}{=} \frac{1}{2\pi}\int_\Gamma dz\, e^{-i\nu} R(z)\, f(0);$$

this formula is, however, not useful. Indeed, for a discontinuous time variable, there exists no Laplace transform and this formula cannot be inverted as usual by an integration over the discontinuous ν. It is, nevertheless, possible to introduce a representation of the propagator U^ν that is very similar to Eqs. (15.23) and (15.24) [6]:

$$U^\nu = \frac{1}{2\pi i}\oint_C dz\, \frac{z^\nu}{z-U}, \quad \nu \geq 0. \qquad (15.32)$$

It is assumed here that the spectrum of U is located inside or on the unit circle around the origin in the complex z-plane [This is the same stability condition as discussed in the continuous case, but in a different guise. It is easily seen that it prevents an asymptotic blow-up of the solution (15.27). The contour of integration is then a circle lying just outside the unit circle (Fig. 15.4.a).

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[6]From here on, for simplicity, we omit the subscript K on the symbol U_K, unless necessary for clarity.
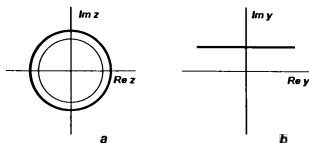
Figure 15.4. Contours of integration in complex z- and y-planes (bold lines).

The proof of this formula is straightforward. It involves an expansion[7] of the geometric series for $(z - U)^{-1}$, followed by the substitution $z \to (1 + \varepsilon)e^{-iy}$, and the limit $\varepsilon \to +0$:

$$\frac{1}{2\pi i} \oint_C dz \, \frac{z^\nu}{z - U} = \frac{1}{2\pi i} \sum_{k=0}^{\infty} \oint_C dz \, z^\nu \, z^{-(k+1)} U^k$$
$$= \frac{1}{2\pi} \sum_{k=0}^{\infty} \int_{-\pi}^{\pi} dy \, e^{-i(\nu - k)y} U^k = \sum_{k=0}^{\infty} \delta_{\nu,k} U^k = U^\nu.$$

From the third expression above, we may derive an alternative form:

$$U^\nu = \frac{1}{2\pi} \int_{\Gamma'} dy \, e^{-i(\nu+1)y} \frac{1}{e^{-iy} - U} \tag{15.33}$$

The contour Γ' in the y-plane is a straight segment: $[-\pi + i\gamma, \ \pi + i\gamma]$ lying above all singularities; it is shown in Fig. 15.4.b. We have thus obtained two equivalent representations of the propagator (or of the Perron-Frobenius operator, for $\nu = 1$), both of which introduce an operator similar to the resolvent (15.24).

We now determine the Perron-Frobenius operator for the standard map (15.5), written in the form:

$$T: \left\{ \begin{array}{l} x' = x - \dfrac{K}{2\pi} \sin 2\pi\theta \\[2mm] \theta' = \theta + x' \end{array} \right. \tag{15.34}$$

---

[7] From the stability condition it follows that one can consider $z > \|U\|$, where the right hand side represents the norm of the operator U.

The inverse standard map is easily obtained by expressing (x, θ) in terms of (x', θ') from the previous equation:

$$T^{-1}: \begin{cases} x = x' + \dfrac{K}{2\pi} \sin 2\pi(\theta' - x') \\ \theta = \theta' - x' \end{cases} \tag{15.35}$$

We now determine the Perron-Frobenius operator from (15.28) combined with (15.31) and (15.35):

$$\begin{aligned} f[x, \theta; \nu] &= U f[x, \theta; \nu - 1] \\ &= f\left[x + \frac{K}{2\pi} \sin 2\pi(\theta - x), \theta - x; \nu - 1\right] \end{aligned} \tag{15.36}$$

The Perron-Frobenius operator can thus be expressed in terms of finite displacement operators, as follows:

$$U = \exp\left(-x\frac{\partial}{\partial \theta}\right) \exp\left(\frac{K}{2\pi} \sin 2\pi\theta \frac{\partial}{\partial x}\right). \tag{15.37}$$

[the order of the factors is, of course, important]. We thus obtained an explicit expression of the Perron-Frobenius operator that governs the evolution of the phase space distribution function under the standard map.

The analysis of the distribution function in the strongly chaotic regime is most conveniently done in a *Fourier representation*. For this purpose, we first need to fix the limits of our system. There is no problem for the angular variable: the distribution function, like all physical quantities must be one-valued, hence 1-periodic in θ. The phase space can thus be limited, for instance, to the domain $\left[-\frac{1}{2} < \theta \leq \frac{1}{2}\right]$ (or to any other domain of total length = 1). As for the x variable, we note that for $K > K_c$, the whole range of x is accessible to the chaotic orbits. We thus consider first an (artificial) finite domain: $\left[-\frac{L}{2} < x < \frac{L}{2}\right]$; at the end, we let $L \to \infty$.

The Fourier transformation formulae are defined as follows in our case:

$$f(x, \theta; \nu) = L^{-1} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \exp\left[2\pi i\left(\frac{n}{L}x + m\theta\right)\right] \widetilde{f}(n, m; \nu),$$

$$\widetilde{f}(n, m; \nu) = \int_{-L/2}^{L/2} dx \int_{-1/2}^{1/2} d\theta \exp\left[-2\pi i\left(\frac{n}{L}x + m\theta\right)\right] f(x, \theta; \nu). \tag{15.38}$$

We now calculate the matrix elements of the Perron-Frobenius operator:

$$\langle n, m |U| n', m'\rangle$$
$$= L^{-1} \int_{-L/2}^{L/2} dx \int_{-1/2}^{1/2} d\theta \exp\left[-2\pi i\left(\frac{n}{L}x + m\theta\right)\right] U \exp\left[2\pi i\left(\frac{n'}{L}x + m'\theta\right)\right]$$

Using (15.37) and the well-known identity:

$$\exp\left(iz\sin\varphi\right) = \sum_l e^{il\varphi} J_l(z), \tag{15.39}$$

the matrix element is easily evaluated as:

$$\langle n, m | U | n', m' \rangle = \sum_l \delta_{m', m-l} \, \delta_{n', n+(m'+l)N} \, J_l\left[K\left(\frac{n}{L} + m\right)\right]. \tag{15.40}$$

We now consider the limit of an infinite extension in the x-direction, $L \to \infty$. In this case, we make the replacement $\frac{n}{L} \to q$, which is considered as a continuous variable; as a result:

$$L^{-1} \sum_n \to \int dq, \qquad L\delta_{n,n'} \to \delta(q - q'),$$

and $\tilde{\tilde{f}}(n, m; \nu) \to \tilde{f}(q, m; \nu)$, a function of the continuous variable q. The transformation formulae (15.38) now become:

$$
\begin{aligned}
f(x, \theta; \nu) &= \int_{-\infty}^{\infty} dq \sum_{m=-\infty}^{\infty} \exp\left[2\pi i\left(qx + m\theta\right)\right] \tilde{f}(q, m; \nu), \\
\tilde{f}(q, m; \nu) &= \int_{-\infty}^{\infty} dx \int_{-1/2}^{1/2} d\theta \, \exp\left[-2\pi i\left(qx + m\theta\right)\right] f(x, \theta; \nu). \tag{15.41}
\end{aligned}
$$

We also note the following representation of the Dirac δ-function (note the location of the 2π factors!):

$$\int_{-\infty}^{\infty} dz \, e^{2\pi i z x} = \delta(x). \tag{15.42}$$

The law of evolution in Fourier space then becomes:

$$\tilde{f}(q, m; \nu) = \int_{-\infty}^{\infty} dq' \sum_{m'=-\infty}^{\infty} \langle q, m | U | q', m' \rangle \, \tilde{f}(q', m'; \nu - 1). \tag{15.43}$$

The expression of the matrix elements of the Perron-Frobenius operator becomes:

$$(q, m | U | q', m') = \sum_l \delta_{m', m-l} \, \delta\left(q' - q - m' - l\right) J_{m-m'}(q'K),$$

which is trivially summed on l:

$$(q, m | U | q', m') = \delta\left(q' - q - m\right) J_{m-m'}(q'K). \tag{15.44}$$

The iteration of Eq. (15.43) yields the following expression for the solution of the initial value problem: [8]

$$\tilde{f}(q, m; \nu) = \int_{-\infty}^{\infty} dq' \sum_{m'=-\infty}^{\infty} \langle q, m | U^{\nu} | q', m' \rangle \ \tilde{f}(q', m'; 0). \tag{15.45}$$

We now possess all the necessary tools for an asymptotic analysis of the evolution in the standard map.

15.3 The Diffusive Regime

It has been known for a long time that the standard map dynamics, in the limit of large stochasticity parameter $K \gg K_c$ and for long times $t \to \infty$, exhibits a *diffusive behaviour*. The corresponding anomalous diffusion coefficient was first derived by RECHESTER and WHITE in 1980. In a recent, not very well-known work, HASEGAWA and SAPHIR, 1991, derived these results very directly, using the general methods of non-equilibrium statistical mechanics. We shall essentially follow the arguments of this important work in the present section.

The object of interest here will be the *density profile* $n(x; \nu)$ [and its Fourier transform $\tilde{n}(q; \nu)$], related to the phase space distribution as follows:

$$n(x; \nu) = \int_{-1/2}^{1/2} d\theta \, f(x, \theta; \nu). \tag{15.46}$$

The Fourier transform of the density profile is simply the Fourier transform of the distribution function for $m = 0$:

$$\tilde{n}(q; \nu) = \tilde{f}(q, m = 0; \nu). \tag{15.47}$$

If the dynamics were diffusive, the density profile (in continuous time) would obey a diffusion equation which, in Fourier space, would have the following form:

$$\partial_t \tilde{n}(q; t) = -D \, q^2 \, \tilde{n}(q; t), \tag{15.48}$$

(because the Fourier transform of ∇^2 is $-q^2$). The solution of this equation, using the notation (15.47), is (for $t = \nu$):

$$\tilde{f}(q, 0; \nu) = e^{-Dq^2\nu} \, \tilde{f}(q, 0; 0). \tag{15.49}$$

We note, as in Sec. 15.3, that the differential equation (15.48), like (15.19), has no equivalent for a discrete map; its solution (15.49), however, like (15.25), remains

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[8]It should be noted that the matrix element of the propagator U^{ν} is not *simply* related to the Perron-Frobenius matrix element (15.44)!

meaningful for discrete values of the time: $t = \nu$. On the other hand, the exact evolution of the density profile under the standard map is given by Eq. (15.45):

$$\bar{f}(q,0;\nu) = \int_{-\infty}^{\infty} dq' \sum_{m'=-\infty}^{\infty} \langle q,0 \, |U^\nu| \, q',m'\rangle \, \bar{f}(q',m';0). \tag{15.50}$$

This equation is, at first sight, very different from (15.49), mainly for two reasons:

- it is not a closed equation for the density profile: $\bar{f}(q,0;\nu)$ is connected to $\bar{f}(q',m';\nu)$ with all possible values of q',m';

- the ν-dependence of the propagator is certainly not a simple exponential, in general.

In order to prove the existence of a diffusive regime, we should be able to show that, in some parameter domain, the propagator tends to the following asymptotic form, as $\nu \to \infty$:

$$\langle q,0 \, |U^\nu| \, q',m'\rangle \stackrel{\sim}{\sim} \delta_{m',0}\delta(q-q')\,e^{-Dq^2\nu}. \tag{15.51}$$

As mentioned above, the relation between the propagator and the Perron-Frobenius operator is not a simple one; in the resolvent representation, however, the time-dependence can be written very explicitly (under an integral!). Eqs. (15.50) and (15.32) yield:

$$\bar{f}(q,m;\nu) = \frac{1}{2\pi i} \oint dz \int dq'$$
$$\times \sum_{m'=-\infty}^{\infty} \left\langle q,m \left| z\,(z-U)^{-1} \right| q',m' \right\rangle \bar{f}(q',m';0). \tag{15.52}$$

The asymptotic analysis of this expression is most easily performed by adapting to the present problem a methodology that has been introduced a long time ago in statistical mechanics. This procedure first requires the definition of a particular state (or group of states) that is singled out as being "relevant" for some reason[9]; all the other states will be called "irrelevant". In the present problem, given Eqs. (15.49), (15.51), it is convenient to single out the state corresponding to the Fourier component of radial wave vector q and angular wave number $m = 0$ of the distribution function. We then introduce a projection operator P that picks out this relevant state from the complete distribution function, and denote by Q its complement, which projects on the irrelevant states:

---

[9]In statistical mechanics one chooses the "vacuum" state, i.e. a state of a many-particle system in which there are no statistical correlations.

$$P = |q,0\rangle \langle q,0|, \qquad Q = I - P. \tag{15.53}$$

where I is the identity operator. Like any projection operators, P and Q are mutually orthogonal, idempotent operators

$$I = P + Q, \qquad P^2 = P, \qquad Q^2 = Q, \qquad PQ = QP = 0. \tag{15.54}$$

The definition of this relevant state allows us to decompose identically the Perron-Frobenius operator (or any other operator!) into a sum of four terms:

$$U = PUP + QUP + PUQ + QUQ \tag{15.55}$$

The meaning of the terms is obvious: the first term represents a (single-step) diagonal transition produced by U from the relevant state to itself; the next one is a (single-step) transition (from right to left) from the relevant state to an irrelevant one, etc.

The next step consists of using a non-trivial representation of the resolvent $(z - U)^{-1}$ associated with the choice of the relevant state. In order not to burden the presentation, we give the proof of this formula in the Appendix:

$$\frac{1}{z - U} = [P + QC(z)P]\frac{1}{z - P\mathcal{E}(z)P}[P + P\mathcal{D}(z)C] + QP(z)Q. \tag{15.56}$$

The operators appearing here are defined as follows. The last term in the right hand side is called:[10]

Propagation fragment:

$$Q\mathcal{P}(z)Q = Q\frac{1}{z - QUQ}Q \tag{15.57}$$

All other operators can be expressed in terms of this one, as follows:

Diagonal fragment:

$$P\mathcal{E}(z)P = PUP + PUQ\mathcal{P}(z)QUP, \tag{15.58}$$

Creation fragment:

$$QC(z)P = Q\mathcal{P}(z)QUP, \tag{15.59}$$

Destruction fragment:

$$P\mathcal{D}(z)Q = PUQ\mathcal{P}(z)Q, \tag{15.60}$$

---

[10]The names of the operators are taken directly from statistical mechanics, where they refer to creation, destruction or propagation of correlations.

The detailed meaning of these operators appears from their derivation given in the Appendix. We may, however, briefly describe their action as follows. The resolvent $(z - U)^{-1}$ is related to a many-step transition from an initial (right) to a final (left) state. The one-step transition operator (Perron-Frobenius) was decomposed in (15.55) into transitions to and from relevant or irrelevant states; Eq. (15.56) is a similar decomposition of the resolvent, with some constraints which make the representation unambiguous. Thus, the propagation fragment represents a multi-step transition from an irrelevant to an irrelevant state, *without ever passing through any relevant state*. The creation (destruction) fragments represent similar transitions from a relevant (irrelevant) state to an irrelevant (relevant) state without passing through a relevant state. The diagonal fragment represents a transition from relevant to relevant state, without passing through the relevant state.

The object of our study is the density profile $\bar{n}(q; \nu) = \bar{f}(q, 0; \nu)$, which corresponds precisely to the relevant state. For its evaluation by Eqs. (15.52) and (15.56), we only need the contribution of the resolvent to the relevant part of the distribution function:

$$P \frac{1}{z - U} = P \frac{1}{z - P\mathcal{E}(z)P} [P + P\mathcal{D}(z)Q] \qquad (15.61)$$

We begin our study by evaluating the diagonal fragment (15.58). We note, using (15.44) that:

$$\langle q, 0 | U | q', 0 \rangle = \delta(q - q') \, J_0(qK)$$

hence:

$$PUP = J_0(qK) \qquad (15.62)$$

Next, we evaluate the second term in (15.58), by expanding the geometric series:

$$PUQ\mathcal{P}(z)QUP = PUQ \frac{1}{z - QUQ} QUP$$

$$= PUQ \sum_j z^{-j-1} (QUQ)^j QUP \equiv \sum_j b_j(z). \qquad (15.63)$$

It is rather easily checked that the term $j = 0$ contributes zero (because it turns out to be impossible to go from $(q, 0)$ to $(q, 0)$ in two steps without passing through the relevant state. As an example of the calculations, we evaluate the term $b_1(z)$, using Eq. (15.44):

$$b_1(z)$$
$$= z^{-2} \int dq_1 \int dq_2 \sum_{m_1 \neq 0} \sum_{m_3 \neq 0} \langle q, 0 | U | q_1, m_1 \rangle \langle q_1, m_1 | U | q_2, m_2 \rangle \langle q_2, m_2 | U | q, 0 \rangle$$
$$= z^{-2} \int dq_1 \int dq_2 \sum_{m_1 \neq 0} \sum_{m_3 \neq 0} \delta(q_1 - q) J_{-m_1}(q_1 K)$$
$$\times \delta(q_1 - q_2 - m_1) J_{m_1 - m_2}(q_2 K) \delta(q - q_2 - m_2) J_{m_2}(qK).$$

Performing the q-integrations, we obtain:

$$b_1(z) = z^{-2} \sum_{m_1 \neq 0} \sum_{m_2 \neq 0} \delta(m_1 + m_2) J_{-m_1}(qK) J_{m_1 - m_2} [(q + m_1)K] J_{m_2}(qK)$$

$$(15.64)$$

An alternative form is:

$$b_1(z) = z^{-2} \sum_{m \neq 0} J_m^2(qK) J_{2m} [(-q + m)K] \tag{15.65}$$

This result can be easily extended to higher orders. Combining Eqs. (15.58), (15.62), (15.63) and the generalization of (15.64), we obtain the following expression for the diagonal fragment:

$$P\mathcal{E}(z)P = J_0(qK) + \sum_{n=2}^{\infty} z^{-n} \sum_{m_1} \dots \sum_{m_n} \delta(m_1 + m_2 + \dots + m_n)$$
$$\times J_{-m_1}(qK) \left\{ \prod_{j=1}^{n-1} J_{m_j - m_{j+1}} \left[\left(q - \sum_{l=1}^{j} m_l \right) K \right] \right\} J_{m_n}(qK).$$

$$(15.66)$$

This is an exact result; although not very transparent, it provides the starting point for an asymptotic analysis. In order to identify an interesting (and mathematically tractable) domain, we introduce the following crucial assumptions.

A) The system is in a *strongly chaotic regime*; this implies that any phase space structures (islands,...) are very small and very rare:

$$\frac{1}{\sqrt{K}} \ll 1. \tag{15.67}$$

B) We consider the evolution over *very large length scales*, i.e., for very small wave vectors. Specifically, we assume:

$$qK \ll 1. \tag{15.68}$$

We now consider Eqs. (15.62), (15.64) - (15.66): they all contain products of Bessel functions. These functions depend on two types of arguments. Some of them depend on qK which, by (15.68) is very small. The others contain arguments of the form $(-qK + \sum mK)$, where the m's are non-zero integers. Hence, qK is very small by (15.68), but $(\sum m) K$ is very large by (15.67). The two types of Bessel functions must therefore be expanded differently: the former for small arguments,

$$J_n(x) = \left(\tfrac{1}{2}x\right)^n \frac{1}{n!} \left[1 - \frac{\left(\tfrac{1}{2}x\right)^2}{1(n+1)} + \frac{\left(\tfrac{1}{2}x\right)^4}{1 \cdot 2(n+1)(n+2)} - \dots\right], \tag{15.69}$$

and the latter for large arguments,

$$J_n(x) = \sqrt{\frac{2}{\pi x}} \left[\cos\left(x - n\frac{\pi}{2} - \frac{\pi}{4}\right) + O\left(\frac{1}{x}\right)\right]. \tag{15.70}$$

The diagonal element of the Perron-Frobenius operator is then simply:

$$PUP = J_0(qK) \sim 1 - \frac{1}{4}(qK)^2 + \frac{1}{4 \cdot 16}(qK)^4 - \dots \tag{15.71}$$

Consider now $b_1(z)$, Eq. (15.65); it is expanded as follows:

$$
\begin{aligned}
b_1(z) \sim \; & z^{-2} \sum_{m \neq 0} \left\{\left(\tfrac{1}{2}qK\right)^m \left[\frac{1}{m!} + O\left(qK\right)^{m+1}\right]\right\}^2 \\
& \times \sqrt{\frac{2}{\pi m K}} \left[\cos\left(mK - 2m\frac{\pi}{2} - \frac{\pi}{4}\right) + O\left(\frac{1}{mK}\right)\right]
\end{aligned}
\tag{15.72}
$$

Clearly, the dominant terms are $m = \pm 1$. We also note that the higher order $b_j(z)$, with $j > 1$ yield smaller contributions: it is seen in Eq. (15.66) that they contain additional Bessel functions of the type $J_m(qK - \sum mK)$, which introduce additional small factors $K^{-1/2}$. We now consider the expression for the denominator in Eq. (15.61). To dominant order, in the regime defined by Eqs. (15.67), (15.68) we find, using (15.58), (15.63):

$$
\begin{aligned}
z - P\mathcal{E}(z)P \; &\approx \; z - PUP - b_1(z) \\
&\sim \; z - \left[1 - \frac{1}{4}q^2K^2 + \frac{1}{2z^2}q^2K^2\sqrt{\frac{2}{\pi K}}\cos\left(K - \frac{5}{4}\pi\right)\right].
\end{aligned}
\tag{15.73}
$$

We thus obtain, in the present regime:

$$P \frac{1}{z-U} = P \frac{1}{z - P\mathcal{E}(z)P} P. \tag{15.74}$$

It is now easily checked that in Eq. (15.61) the contribution of the destruction fragment $PD(z)Q$ is negligible. Indeed, it introduces at least one operator PUQ whose matrix element introduces an additional Bessel function $J_m(qK)$, with $m \neq 0$, into Eq. (15.74), hence [see Eq. (15.69)] an additional small factor (qK).

Thus, in the regime (15.67), (15.68), the dominant contribution to the resolvent operator is diagonal (relevant → relevant). This is already a necessary feature for the validity of Eq. (15.51). Eq. (15.52) then reduces to a closed equation for the density profile:

$$\tilde{n}(q; \nu) = \frac{1}{2\pi i} \oint dz \left\langle q, 0 \left| \frac{z^\nu}{z - P\mathcal{E}(z)P} \right| q, 0 \right\rangle \tilde{n}(q; 0). \tag{15.75}$$

The integral can be evaluated by the method of residues. For its application, we need to know the location of the poles of the integrand, i.e., the location of the zeroes of the denominator in (15.75). We introduce the abbreviations:

$$a = \frac{qK}{2}, \quad b = \sqrt{\frac{2}{\pi K}} \cos\left(K - \frac{5}{4}\pi\right)$$

Annulling the denominator (15.73) yields a cubic equation:

$$z^3 - (1 - a^2)z^2 - 2a^2 b = 0. \tag{15.76}$$

It is easily seen that this polynomial possesses a single root of zeroth order, and two roots that are small ($\propto a$, or $\propto b$). Writing the roots as $z_0 = z_{00} + a^2 z_{20}$, one finds the large root as follows:

$$z_0 = 1 - \frac{q^2 K^2}{4} \left[1 - 2\sqrt{\frac{2}{\pi K}} \cos\left(K - \frac{5}{4}\pi\right) \right] + \dots \tag{15.77}$$

This expression can thus be identified, to dominant order, to the expansion of the following exponential:

$$z_0 \simeq \exp\left\{ -q^2 \frac{K^2}{4} \left[1 - 2\sqrt{\frac{2}{\pi K}} \cos\left(K - \frac{5}{4}\pi\right) \right] \right\} \tag{15.78}$$

We now define the following quantity:

$$D = \frac{K^2}{4} \left[1 - 2\sqrt{\frac{2}{\pi K}} \cos\left(K - \frac{5}{4}\pi\right) \right]. \tag{15.79}$$

This also be written by reconstructing a Bessel function, as follows:

$$D = \frac{K^2}{4} \left[1 - 2 J_2(K) \right]. \tag{15.80}$$

Returning now to Eq. (15.75), and using (15.73), we approximate the integral by the residue at the dominant pole:

$$
\begin{aligned}
\tilde{n}(q; \nu) &\approx \frac{1}{2\pi i} \oint dz \, \frac{z^\nu}{z - \left[1 - \frac{1}{4} q^2 K^2 + \frac{1}{2} q^2 K^2 \sqrt{\frac{2}{\pi K}} \cos\left(K - \frac{5}{4}\pi \right) \right]} \, \tilde{n}(q; 0) \\
&\approx \frac{1}{2\pi i} \oint dz \, \frac{z^\nu}{z - \exp\left(-q^2 D \right)} \, \tilde{n}(q; 0)
\end{aligned}
$$

and finally:

$$\tilde{n}(q; \nu) \sim \exp\left(-q^2 D \nu \right) \tilde{n}(q; 0). \tag{15.81}$$

This result is equivalent to (15.49): it thus completes the proof of our assertion, which we summarize as follows. *In the regime defined by Eqs. (15.67) (strong stochasticity) and (15.68) (long spatial scale) the asymptotic evolution produced by the standard map is a* DIFFUSION PROCESS. This remarkable result was first obtained by RECHESTER and WHITE in 1980.

We now discuss the expression of the diffusion coefficient (15.79). It appears as a sum of two terms; because of (15.67) the second one is a small correction to the first one, D_{QL}:

$$D_{QL} = \frac{1}{4} K^2. \tag{15.82}$$

This is called the *quasilinear diffusion coefficient* (a name originating from the theory of diffusion in a turbulent plasma). It is a typical example of an ANOMALOUS DIFFUSION COEFFICIENT (according to the terminology defined in Sec. 14.2). In other words, the diffusion exponent $\alpha = 1$ meaning that the regime is diffusive, but the mechanism of the process is entirely non-collisional: it is solely determined by the stochasticity parameter K.

For large, but somewhat smaller values of the stochasticity parameter, the second term represents a first correction, of order $K^{-1/2}$. Interestingly, this correction is an *oscillating function* of K, as can be seen in Fig. 15.5. The oscillations are usually interpreted as the effect of the *islands*, although there is, at present, no formal proof of this statement.
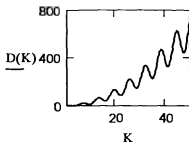
Figure 15.5. Standard map diffusion coefficient.

Another feature of the standard map is absent from the theory. Numerical simulations show that the diffusion coefficient has several very sharp maxima ($\sim \infty$) for certain values of K. It is shown that these divergences are connected to the accelerator modes, briefly mentioned in Sec. 15.1. These produce a *superdiffusive behaviour* of the standard map. This is, however, not a generic feature of the two-dimensional area preserving maps, but rather a specific property of the standard map. We discuss very briefly this problem at the end of Sec. 15.4.

15.4   The Subdiffusive Regime

In the previous chapter we studied the diffusive properties of systems of "particles" whose dynamics is governed by the standard map. This implies that the stochasticity parameter K has a value above the critical value K_c corresponding to the destruction of the most robust KAM barrier. We now study the dynamics of these systems for $K < K_c$. In many applications this is a more important regime. In particular, in the problem of magnetic line dynamics, a confining geometry of the magnetic field is only possible for $K < K_c$: in the opposite case there would exist an infinite number of lines that are not stopped by any KAM barrier and would therefore (physically) hit the wall of the tokamak.

The regime under discussion corresponds to a situation of PARTIALLY CHAOTIC DYNAMICS. The phase space contains three kinds of objects: *island chains*, *KAM barriers* and *chaotic orbits*, illustrated in Fig. 15.6.
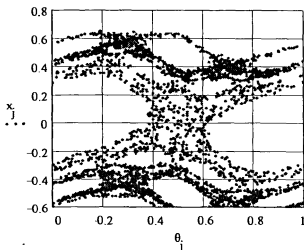
Figure 15.6. A chaotic orbit for $K \approx K_c$.

The golden KAM is an absolute barrier in this case. Moreover, depending on the value of K, there may be additional barriers defining regions in phase space whose boundaries cannot be crossed by any chaotic orbit. In Fig. 15.6 there are three clearly visible regions differing by the density of the phase points: the boundaries between them are *cantori*. The orbit starting in the upper part $[r_0 = 0.3, \theta_0 = 0.75]$ had to wait for a relatively long time before finding its way through a hole in the cantorus which is bounding it below. This suggests a very peculiar type of motion of the particle. It cannot wander at random to any point of phase space at any time. Rather, it *sticks* to a certain region near an island chain for a certain time (which can be very long), then jumps to another region, where it sticks again for many iterations, etc. This feature will become even clearer n the forthcoming developments.

In the situation represented in Fig. 15.6 there appear clearly *four "main" island chains* that are clearly identifiable by the "large" size of the islands. Clearly, the distinction between "large" and "small" islands is arbitrary. The forthcoming treatment does not depend on where the limit is set, provided the number of "large" islands is specified at the beginning. There are also, of course, secondary islands around each "large" island: these will be, by convention, included into the main island chain (the term "included" will be defined more precisely below).

In the present section, the motion is idealized as follows. At time $t = 0$, a large number of particles is distributed in the phase space. The particles are subdivided into two classes. The *jailed particles* are those whose initial position lies inside an island chain. For all subsequent times they will remain inside the island chain where they started (actually they jump from one island of the chain to another): their number remains constant. The particles in the complementary set, whose initial coordinates are located outside the island chains, are called *active particles*: for $t > 0$ they will fill in all the space between the islands, bounded by two successive KAM barriers. These will be the main object of interest in the forthcoming work. For brevity we agree to call simply "particles" the active particles, unless explicitly stated to the contrary.

We shall study the way in which a set of particles starting with an arbitrary initial distribution in a certain bounded region[11] is eventually dispersed and fills the entire phase space region included between the limiting KAM barriers and the island boundaries (as in Fig. 15.6). Alternatively, assuming the validity of (some kind of) an ergodic property, one may follow a single chaotic trajectory for a long time (i.e. by calculating many iterations of the standard map). In many applications (e.g., the problem of magnetic line diffusion in a tokamak) the main interest lies in a reduced problem, *viz.* the *"diffusion" in the x-direction*. The complete solution of this problem would involve the determination of the *density profile* $n(x;t)$ [for $t = \nu \Delta t$, $\nu \in \mathbb{Z}$]; this quantity is, however, not easily accessible, either analytically or numerically. A good (and usual) indicator of the dispersion is the *mean square displacement*[12] (MSD): $\langle \delta x^2(t) \rangle$. This is easily measured numerically; our purpose here will be to devise an analytical model for its determination.

It is pretty clear *a priori* that the evolution process in the case $K < K_c$ *cannot be diffusive*. Indeed, because of the presence of the KAM barriers, the MSD will necessarily *saturate* asymptotically, as $t \to \infty$. The final value will be essentially the square of the width of the region. This is in contrast with a diffusive process, in which the MSD exhibits an unbounded growth, proportional to time. The effective diffusion coefficient, defined as usual, is thus necessarily zero:

$$D \equiv \tfrac{1}{2} \lim_{t \to \infty} \frac{d}{dt} \left\langle \delta x^2(t) \right\rangle = 0. \qquad (15.83)$$

We are thus in presence of a typical *subdiffusive behaviour*.

This type of behaviour is somewhat analogous to the one described in Sec. 14.2 for de Gennes' "ant in a labyrinth" model. For $p < p_c$, the ants are necessarily trapped in non-percolating, finite clusters and the MSD necessarily saturates, as shown in Eq. (14.4). Here too, below K_c, the orbits are trapped, either in islands, or by KAM

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[11]In the present context, a "bounded region" means a region bounded by two successive KAM barriers.

[12]This quantity will be defined more precisely below.

barriers. The piercing of the last KAM barrier is analogous to the appearance of the infinite cluster in the percolation problem
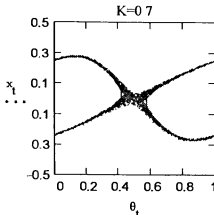

Figure 15.7. A chaotic orbit for $K = 0.7$.

From here on, for the purpose of illustration, we consider a very simple situation which can be solved analytically. The stochasticity parameter is chosen to be well below the critical threshold, but not too small (in order to produce sufficiently large chaotic regions); specifically, we choose $K = 0.7$. The portion of phase space under consideration is taken as the region bounded by the main island around $(0,0)$ and the nearest undestroyed KAM barriers above ($x > 0$) and below ($x < 0$) this island; a typical chaotic orbit is shown in Fig. 15.7.

The interesting problem is to study the dynamics of the approach to the saturated steady state. Numerically, one could study an animated version of Fig. 15.7, in which the points of the orbit appear on the screen in their natural succession. This phase-space representation has an undoubtable aesthetical value; it is, however, not very useful for a quantitative study. A much more interesting representation is the graph of the x-coordinate as a function of (discrete) time t: it provides us with a very different view of the evolution process. The complete graph of x_t vs. t for a long trajectory requires, of course, a *very long* sheet of paper![13] The analysis can be done, however, by using successive short sections of this time series.

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[13]It is very instructive to realize once such a "collage" for a long orbit (say, 25 000 iterations): a look at it is the best way of convincing oneself of the forthcoming arguments.
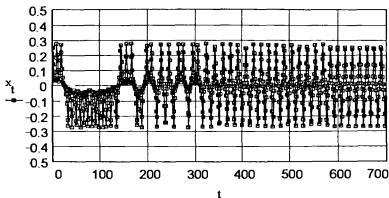
Figure 15.8. Section of time series of the chaotic orbit of Fig. 15.7.

This type of evolution is very peculiar (Fig. 15.8). We see a first period, roughly between $t = 0$ and $t = 30$ where the particle oscillates fairly regularly between two limits ($0 < x < 0.28$); at $t \approx 30$ there is a sudden jump down to $x \approx -0.28$; from $t \approx 30$ and 140 there is an oscillation between -0.28 and 0; then the particle jumps back to $x \approx 0.28$; after several such jumps, it reaches $t \approx 200$, after which it starts oscillating with a double amplitude between $x = -0.28$ and 0.28: this motion lasts from $t = 200$ to $t = 1180$ when a new oscillation in the lower region starts, etc. The situation is adequately described in terms of a set of *basins*. A particle moving on a chaotic orbit starts at time zero in a basin, and remains confined in it for some time; at some instant, it jumps suddenly to another basin and starts oscillating for some time in the latter, after which another sudden jump brings it into another basin, etc. The duration of the sojourn in a basin is extremely variable: it may be as short as 10 iterations or as long as 10000! The times at which the jumps occur do not seem to exhibit any regularity. When looking at a long trajectory, the effect is particularly striking. The basins are clearly located in the (external) neighbourhood of the island chains. The peculiar type of motion is thus a consequence of the *sticking property* of the island chains. Our results show that the influence of a given island can extend very far in phase space (for $K < K_c$), to the point that the whole available phase space for a chaotic orbit can be subdivided into basins connected to the islands. On the other hand, a basin is not defined merely as the whole neighbourhood of an island.

This type of evolution immediately suggests the picture of a CONTINUOUS TIME RANDOM WALK (CTRW). We will consider the evolution in time of the coordinate

x_t. Any given (active) particle remains in a "state", i.e., a basin, for some time, then jumps abruptly to another "state", etc. We shall not be interested in the details of the motion within a given basin. Rather, we assume that the motion, starting at a given initial value, is described *statistically*: the motion is then completely defined by the specification of three features: *the location of the relevant basins in phase space, the probability of a sojourn of length t in a given basin, and the transition probability between two basins.* All these quantities will be precisely defined below.

The first point mentioned above, i.e., the location of the *relevant* basins, depends on the value of the stochasticity parameter and on the initial condition. In the example chosen here, the relevant region is bounded by the main island and by two KAM barriers. One can recognize in Fig. 15.7, near the boundary of the main island, a number of small secondary islands. In the time series, they do not, however, appear as a distinct entity (with a well defined attached basin). They are therefore not counted separately, but rather are supposed to belong to the chaotic region.

In any time series, as in Fig. 15.8, it clearly appears that the x-coordinate sojourns successively in three regions: these are the relevant *basins* for $K = 0.7$ and for the region of phase space chosen here. This situation clarifies our previous remark: the basins are not necessarily simply related, one-to-one, to the island-to-island chains. In the present case here is a *single island* [centered on $(0, 0)$], but there are *three basins*. The latter correspond to the whole island, to the upper half of the island, and to its lower half, respectively. Thus, the basins do not represent a geometrical feature of the phase space, but rather a *dynamical property*, related to the way in which the orbit is covered in the course of time.

Having identified the relevant basins, we now construct a CTRW model describing approximately this dynamics. The procedure is based on an adaptation of the arguments of Chap. 12. We recall that we are only considering here the distribution of active particles among the relevant basins. The latter will be labelled by a latin subscript, e.g., $m = 1, 2, ..., M$, where M is the number of relevant basins in the problem. In our example, $M = 3$; the labels are chosen (conventionally) as follows:

- $m = 1$: whole island basin;

- $m = 2$: upper half island basin;

- $m = 3$: lower half island basin.

The random walk (i.e., the "dynamics") is completely determined by the quantities $n_m(t)$: the probability of finding a particle in basin m at time t. These quantities can be considered as the components of a M-component vector $\mathbf{n}(t)$. In our example:

$$\mathbf{n}(t) = [n_1(t), n_2(t), n_3(t)]. \tag{15.84}$$

We also use the abbreviated notation $\mathbf{n}^0 \equiv \mathbf{n}(0)$ [or $n_m^0 \equiv n_m(0)$ for the components] for the initial condition. We have thus deliberately smoothed the description of the motion, retaining only features that are relevant for transport theory.

Next, we define the *waiting time distribution (WTD)*. In the "usual" CTRW problem discussed in Chap. 12, there is a single function $\psi(t)$ characterizing completely this quantity. Here, the waiting time distribution can be different in the various basins. We thus define $p_m(t)$ as the *probability that a particle, entering the basin m, makes a transition to another basin after a time t.* It appears that these quantities must be considered as components of a diagonal $M \times M$ matrix, $\mathsf{P}(t)$:

$$\mathsf{P}(t) = \begin{pmatrix} p_1(t) & 0 & 0 \\ 0 & p_2(t) & 0 \\ 0 & 0 & p_3(t) \end{pmatrix}. \tag{15.85}$$

Thus, in general, the matrix elements of $\mathsf{P}(t)$ are

$$\langle m | \mathsf{P}(t) | n \rangle = p_m(t)\, \delta_{mn}. \tag{15.86}$$

The last ingredient necessary for the definition of the CTRW is the *transition probability from basin n to basin m:* these define a matrix F:

$$\langle m | \mathsf{F} | n \rangle = f_{mn}. \tag{15.87}$$

By definition, the diagonal elements are identically zero. It turns out that the matrix is symmetric (but this is not a necessary property!). Thus, in our example we have:

$$\mathsf{F} = \begin{pmatrix} 0 & f_{12} & f_{13} \\ f_{12} & 0 & f_{23} \\ f_{13} & f_{23} & 0 \end{pmatrix}. \tag{15.88}$$

We now start the solution of the problem. We note that the probability that at least one jump has been made out of the basin m during the interval $[0, t]$ is the integral of $p_m(\tau)$ from 0 to t; hence, the probability that a particle, entering basin m at time zero, is still there at time t is:

$$r_m(t) = 1 - \int_0^t d\tau\, p_m(\tau), \tag{15.89}$$

or, performing a Laplace transformation,

$$\hat{r}_m(s) = \frac{1}{s}\left[1 - \hat{p}_m(s)\right].$$

These quantities are grouped into a diagonal matrix [because of (15.86)]:

$$\widehat{R}(s) = \frac{1}{s}\left[1 - \widehat{P}(s)\right].\tag{15.90}$$

Let now $q_m(t)$ be the probability that a particle arrives in basin m just after a jump. Then, the probability $n_m(t)$ is obtained by considering the probability $q_m(\tau)$ of landing in basin m just at time τ, multiplied by the probability that it is still in m at time t, and summed over all intermediate times τ:

$$n_m(t) = \int_0^t d\tau\, r_m(t-\tau)\, q_m(\tau),$$

or, in vector notation and in Laplace representation:

$$\widehat{n}(s) = \frac{1}{s}\left[1 - \widehat{P}(s)\right]\cdot \widehat{q}(s).\tag{15.91}$$

In order to calculate the quantity $q_m(t)$ we consider successively the cases where the particle that started in basin k at $t = 0$ lands in m at time t in j steps. For $j = 1$, the particle remains in basin k for a time t and makes a jump to m at that time; thus:

$$q_m^{(1)}(t) = \sum_k f_{mk}\, p_k(t)\, n_k^0\tag{15.92}$$

For $j = 2$, the particle waits in basin k from $t = 0$ to τ, jumps to basin l, then waits there till t, when it jumps to m:

$$q_m^{(2)}(t) = \sum_{k,l}\int_0^t d\tau\, f_{ml}\, p_l(t-\tau)\, f_{lk}\, p_k(\tau)\, n_k^0$$

$$= \sum_l \int_0^t d\tau\, f_{ml}\, p_l(t-\tau)\, q_l^{(1)}(\tau).$$

This argument is easily generalized for arbitrary j, yielding a recurrence relation:

$$q_m^{(j)}(t) = \sum_k \int_0^t d\tau\, f_{mk}\, p_k(t-\tau)\, q_k^{(j-1)}(\tau),\tag{15.93}$$

which must be solved with the following condition, which ensures the consistency of Eqs. (15.92) and (15.93):

$$q_k^{(0)}(\tau) = n_k^0\,\delta(\tau).\tag{15.94}$$

It is easily checked, using the forms (15.85) and (15.88) that eq. (15.93) is written in matrix form as follows: [14]

---

[14] At this point it clearly appears that the remarkable factorization appearing in (15.95) is ensured by our defining the quantities $p_m(t)$ as components of a diagonal matrix, rather than a vector.

$$\mathbf{q}^{(j)}(t) = \int_0^t d\tau \, \mathsf{F} \cdot \mathsf{P}(t-\tau) \cdot \mathbf{q}^{(j-1)}(\tau). \tag{15.95}$$

In Laplace representation, this equation becomes an algebraic one:

$$\hat{\mathbf{q}}^{(j)}(s) = \mathsf{F} \cdot \widehat{\mathsf{P}}(s) \cdot \hat{\mathbf{q}}^{(j-1)}(s),$$

which is easily solved, yielding:

$$\hat{\mathbf{q}}^{(j)}(s) = \left[\mathsf{F} \cdot \widehat{\mathsf{P}}(s) \right]^j \cdot \mathbf{n}^0.$$

We now sum this result over j in order to obtain the total probability vector $\hat{\mathbf{q}}(s)$:

$$\hat{\mathbf{q}}(s) = \left[\mathsf{I} - \mathsf{F} \cdot \widehat{\mathsf{P}}(s) \right]^{-1} \cdot \mathbf{n}^0. \tag{15.96}$$

Finally, we substitute this result in Eq. (15.91) and obtain the final result:

$$\hat{\mathbf{n}}(s) = \frac{1}{s} \left[\mathsf{I} - \widehat{\mathsf{P}}(s) \right] \cdot \left[\mathsf{I} - \mathsf{F} \cdot \widehat{\mathsf{P}}(s) \right]^{-1} \cdot \mathbf{n}^0. \tag{15.97}$$

This equation provides us with the complete solution of the initial value problem for our CTRW. It is very similar to the MONTROLL-WEISS EQUATION (12.42), adapted to our problem. It expresses the Laplace transform of the probability of the distribution of the particles among basins, in terms of the initial condition $\mathbf{n}^0$ and of the input information expressed by the waiting time distribution $\mathsf{P}(s)$ and the transition probabilities F. An equation of evolution for $\hat{\mathbf{n}}(s)$ is easily derived from (15.97):

$$s \, \hat{\mathbf{n}}(s) - \mathbf{n}^0 = -(\mathsf{I} - \mathsf{F}) \cdot \widehat{\mathsf{Q}}(s) \cdot \hat{\mathbf{n}}(s), \tag{15.98}$$

where:

$$\widehat{\mathsf{Q}}(s) = s \widehat{\mathsf{P}}(s) \cdot \left[\mathsf{I} - \widehat{\mathsf{P}}(s) \right]^{-1}. \tag{15.99}$$

Eq. (15.98) is analogous to Eq. (12.45). By inverse Laplace transformation of (15.98) we obtain a *Non-Markovian equation of evolution* for the distribution vector, similar to the Montroll-Shlesinger equation (12.46):

$$\frac{d\,\mathbf{n}(t)}{dt} = -(\mathsf{I} - \mathsf{F}) \cdot \int_0^t d\tau \, \mathsf{Q}(\tau) \cdot \mathbf{n}(t-\tau), \tag{15.100}$$

which is to be solved with the initial condition $\mathbf{n}(0) = \mathbf{n}^0$. These equations are quite generally valid, for an arbitrary CTRW, with an arbitrary number of basins.

We now specialize the solution to our simple three-basin situation. The CTRW that models the standard map dynamics is defined by the *transition probability matrix* F and by the *waiting time distribution matrix* $\mathsf{P}(t)$ [which, in turn, determines $\mathsf{Q}(\tau)$].

These quantities are determined from an analysis of several "long" chaotic orbits (say, each of about $N = 25000$ iterations) generated by the standard map. The general idea of the procedure is described below; for the details, the interested reader is referred to the original paper.

Transition probabilities.

For each orbit, every jump from a basin n to a basin m is recorded: the total number of such jumps is denoted by $N_{m\leftarrow n}$. In order to define transition probabilities $f_{m\leftarrow n}$, we note that a particle leaving basin n can only jump in one of the two other basins, hence:

$$\sum_n f_{m\leftarrow n} = 1. \qquad (15.101)$$

Using this normalization condition, we define a first set of empirical transition probabilities as follows:

$$f'_{1\leftarrow 2} = \frac{N_{1\leftarrow 2}}{N_{1\leftarrow 2} + N_{1\leftarrow 3}}, \quad f'_{1\leftarrow 3} = 1 - f'_{1\leftarrow 2}, \quad etc.$$

Next, we note that the exact transition probabilities must also satisfy the following independent normalization, expressing that the particles entering basin m can only originate from one of the two other basins:

$$\sum_m f_{m\leftarrow n} = 1. \qquad (15.102)$$

It is easily checked that this condition is necessary for ensuring the conservation law for the particles at all times:

$$n_1(t) + n_2(t) + n_3(t) = n_1^0 + n_2^0 + n_3^0. \qquad (15.103)$$

Eq. (15.102) allows us to define an alternative set of approximate transition probabilities (for each orbit):

$$f''_{1\leftarrow 2} = \frac{N_{1\leftarrow 2}}{N_{1\leftarrow 2} + N_{3\leftarrow 2}}, \quad f''_{3\leftarrow 2} = 1 - f''_{1\leftarrow 2}, \quad etc.$$

These numbers are slightly different from the corresponding f' 's. Next, the two values are added and divided by two, and the results are averaged over all the orbits considered. It appears that the two sum rules are pretty well satisfied in spite of the rather small statistics. We also note that the matrix is very nearly symmetric.

Finally, we note that, taking into account the standard deviations, this "empirical" matrix is compatible with the simplest choice implying maximum symmetry:

$$f_{m \leftarrow n} = \tfrac{1}{2}, \quad \forall m, \ \forall n \neq m, \quad \text{i.e.:}$$

$$\mathbf{F} \approx \begin{pmatrix} 0 & 0.5 & 0.5 \\ 0.5 & 0 & 0.5 \\ 0.5 & 0.5 & 0 \end{pmatrix} \tag{15.104}$$

The waiting time distribution.

The successive times of sojourn in a given basin m, Δt_m, were measured sequentially in each of the four orbits available. We then determined for each basin m (and for each orbit) the number $N_m^{(q)}$ of occurrences in successive sectors of length 50 comprised between $t = q$ and $t = q + 49$ (e.g., the number of sojourns of length $0 < \Delta t_1 \leq 49$, in basin 1, then the number of sojourns of length $50 \leq \Delta t_1 \leq 99$, etc.): these numbers (for each m and each q) were summed for all orbits. Dividing these numbers by the total number of successive sojourns in basin m, we obtain a histogram, which is an estimate for the waiting time probability in basin m:

$$\hat{p}_m^{(q)} = \frac{N_m^{(q)}}{\sum_q N_m^{(q)}}. \tag{15.105}$$

The quantities $\hat{p}_m^{(q)}$ are plotted vs. q, i.e. vs. time. From their analysis, it appears that the results are compatible with a power law distribution:

$$p_m(t) = A_m \, t^{-1-\alpha_m}, \tag{15.106}$$

with:

$$\alpha_1 \equiv \alpha = 0.3, \qquad A_1 = 10^{0.5},$$
$$\alpha_2 = \alpha_3 \equiv \beta = 0.5, \qquad A_2 = A_3 = 10^{0.6} \tag{15.107}$$

A simple calculation yields the following form for the solution (15.98) in Laplace representation:

$$\hat{n}_1(s) = \frac{1-\hat{p}_1}{s\,\hat{\Delta}} \left[(4 - \hat{p}_2 \hat{p}_3) \, n_1^0 + (2 + \hat{p}_3) \, \hat{p}_2 \, n_2^0 + (2 + \hat{p}_2) \, \hat{p}_3 \, n_3^0 \right], \tag{15.108}$$

with similar expressions for the other functions $\hat{n}_2(s), \hat{n}_3(s)$, and:

$$\hat{\Delta} = 4 - \hat{p}_1\hat{p}_2 - \hat{p}_1\hat{p}_3 - \hat{p}_2\hat{p}_3 - \hat{p}_1\hat{p}_2\hat{p}_3. \qquad (15.109)$$

(all symbols with a hat denote functions of s). We now use the following *asymptotic power laws*, assumed to be valid for $s \to 0$:

$$\hat{p}_m(s) = [1 - B_m\, s^{\alpha_m}], \qquad s \to 0. \qquad (15.110)$$

Their inverse Laplace transforms are given by a Tauberian theorem:

$$p_m(t) = B_m\, \frac{\alpha_m}{\Gamma(1 - \alpha_m)}\, t^{-1-\alpha_m}, \qquad t \to \infty. \qquad (15.111)$$

Thus, choosing:

$$B_m = A_m\, \frac{\Gamma(1 - \alpha_m)}{\alpha_m}, \qquad (15.112)$$

we are in agreement with the empirically determined Eq. (15.106). Using Eqs. (15.108) - (15.110), expanding the result for small s, and performing the inverse Laplace transformation, we find after a lengthy but simple calculation the following result. We abbreviate as C the following constant:

$$C = \frac{B_2}{\Gamma(1 - \beta)},$$

and we define a set of functions $H_{ij}(t)$ as follows:

$$
\begin{aligned}
H_{11}(t) &= 1 - \frac{2b}{\Gamma(1 - \beta + \alpha)}\, t^{-(\beta-\alpha)} + \frac{4b^2}{\Gamma(1 - 2\beta + 2\alpha)}\, t^{-2(\beta-\alpha)} + 2C\, t^{-\beta}, \\
H_{12}(t) &= H_{11}(t) - 2C\, t^{-\beta}, \\
H_{21}(t) &= \frac{b}{\Gamma(1 - \beta + \alpha)}\, t^{-(\beta-\alpha)} - \frac{2b^2}{\Gamma(1 - 2\beta + 2\alpha)}\, t^{-2(\beta-\alpha)} - C\, t^{-\beta}, \\
H_{22}(t) &= H_{21}(t) + \frac{4}{3} C\, t^{-\beta}, \\
H_{23}(t) &= H_{21}(t) + \frac{2}{3} C\, t^{\,\beta}; \qquad (15.113)
\end{aligned}
$$

here $b = B_2/B_1$. The asymptotic solution of the CTRW problem is then:

$$
\begin{aligned}
n_1(t) &= H_{11}(t)\, n_1^0 + H_{12}(t)\, \left[n_2^0 + n_3^0\right], \\
n_2(t) &= H_{21}(t)\, n_1^0 + H_{22}(t)\, n_2^0 + H_{23}(t)\, n_3^0, \\
n_3(t) &= H_{21}(t)\, n_1^0 + H_{23}(t)\, n_2^0 + H_{22}(t)\, n_3^0. \qquad (15.114)
\end{aligned}
$$

The conservation law (15.103) is easily checked. The behaviour of the solution is understood from Fig. 15.9 (In this and the following figures we take: $n_1^0 = 0.5$, $n_2^0 = 0.05$, $n_3^0 = 0.45$).
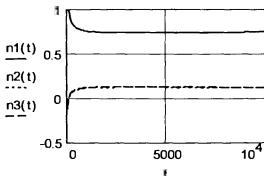

Figure 15.9. Time evolution of probabilities.

For very short times, we see a very rapid evolution; this region is, however, irrelevant. Indeed, in this range $n_1(t) > 1$ and $n_2(t), n_3(t) < 0$. The asymptotic regime expressed by Eqs. (15.114) begins to be valid, at least, for $t > 200$, when all probabilities are in the physical domain. Next, we note that the evolution is *strikingly slow*. Indeed, the asymptotic behaviour of the density profiles is $\propto t^{-(\beta-\alpha)} = t^{-0.2}$. The long time behaviour is thus better seen on a semi-log plot, showing $n_i(t)$ vs. $\log t$ (Fig. 15.10). It is easily shown from (15.114) that the final values of the probabilities are:

$$n_1^\infty = 1, \quad n_2^\infty = 0, \quad n_3^\infty = 0 \qquad (15.115)$$

Note that this asymptotic solution results from the inequality: $\alpha < \beta$. It is physically rather reasonable that after a long time all the particles end up in the basin corresponding to the entire island.

Next, we note that the curves representing $n_2(t)$ and $n_3(t)$ are indistinguishable. Indeed, it can be seen from Eqs. (15.113) that the corresponding functions only differ by the terms proportional to $t^{-\beta}$, which are the most rapidly decaying ones. Thus, for sufficiently long times, the two curves coincide. Finally, by considering various values for n_i^0, it is found that the asymptotic evolution given by Eqs. (15.114) is remarkably insensitive to the initial conditions: after, say, $t = 1000$, all curves are practically the same. On the other hand, as for all asymptotic approximations, the solution cannot be extrapolated back to $t = 0$.
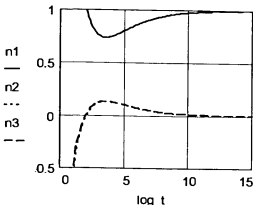
Figure 15.10. Evolution of probabilities vs. log t.

In order to determine the nature of the "diffusion" process, we now determine the evolution of the *mean square displacement (MSD)* as a function of time. It is naturally defined as follows:

$$\Sigma(t) = \sum_{j=1}^{3} \sigma_j^2 \, n_j(t), \qquad (15.116)$$

where σ_j is the width of the basin j, which is determined graphically from the orbits plotted as in Fig. 15.8. Indeed, during its sojourn in basin j, the particle oscillates with an amplitude of order σ_j. The following values are obtained:

$$\sigma_1 = 0.56, \quad \sigma_2 = \sigma_3 = 0.26. \qquad (15.117)$$

Given the slowness of the process, this function is again plotted *vs.* log t in Fig. 15.11.
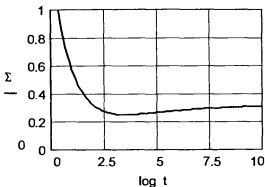
Figure 15.11. Evolution of the mean square displacement.

The initial descending section of the curve is irrelevant, because it lies in the unphysical range (i.e., the range where the probabilities lie outside the physical domain [0.1] and the asymptotic approximation is invalid). After the "ghost minimum" (which corresponds roughly to $t \approx 250$ for all initial conditions) the MSD increases very slowly towards an *asymptotic saturation* value Σ^∞, which is easily understood from Eqs. (15.115) and (15.116):

$$\Sigma^\infty = \sigma_1^2 = 0.314 \qquad (15.118)$$

We now consider the *running diffusion coefficient* $D(t)$, defined in the usual way:

$$D(t) = \tfrac{1}{2} \frac{d}{dt} \Sigma(t). \qquad (15.119)$$

Its graph is shown in Fig. 15.12 (plotted again vs. $\log t$).

Only the relevant, (i.e., positive) part of the function is shown. The running diffusion coefficient is very small at all times ($\approx 10^{-7}$); after a maximum, it decays to zero as $t \to \infty$.

The asymptotic vanishing of the running diffusion coefficient and the corresponding saturation of the mean square displacement are the signature of a subdiffusive behaviour of the standard map dynamics in the subcritical domain $K < K_c$, i.e., in a regime of incomplete chaos. This kind of behaviour is certainly not unexpected; the only less obvious feature is the extreme slowness of the evolution. This shows that the stickiness of the islands is a very strong factor determining the slowing down of the evolution process.
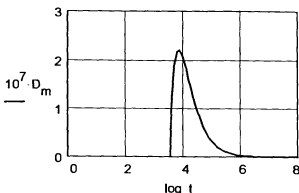
Figure 15.12. Running diffusion coefficient.

It is interesting to note that a *specific property* of the standard map (not shared by the general twist maps) also produces a different type of strange transport. It was mentioned in Sec. 15.1 that, for certain values of K ($> K_c$) there exist *accelerator modes* around which there exist islands, just like around any cycle. Because of their *stickiness*, the chaotic orbits lying near an accelerator mode are swept along in the x-direction. The result is a SUPERDIFFUSIVE REGIME. Thus, stickiness can produce both subdiffusive and superdiffusive behaviour. We do not discuss further this interesting, but very specific phenomenon.

15.5   Appendix. Transformation of the Resolvent

We start with the following trivial identity for the resolvent[15] $R(z) \equiv R = (z - U)^{-1}$:

$$\frac{1}{z - U} = \frac{1}{z} + \frac{1}{z} U \frac{1}{z - U}.$$

Introducing the notation[16] $R_0(z) \equiv R_0 = z^{-1}$, we rewrite this as follows:

---

[15]Most often, in the present appendix, we omit writing the variable z on which the operators depend.

[16]Unlike the corresponding operator in (continuous time) statistical mechanics, the operator $R_0(z)$ is NOT the unperturbed resolvent (the latter is obtained by setting $K = 0$ in the expression of U). R_0 does, however, play the same formal role as the latter in the forthcoming developments.

$$R = R_0 + R_0 U R. \qquad (15.120)$$

The following derivation is a straightforward adaptation of the treatment given in Chap. 16 of Ref. RB-2 (see BN1). We defined in Eq. (15.53) a *"relevant state"* and consequently a decomposition of the unit operator into a sum of two mutually orthogonal projection operators: $I = P + Q$ [Eq. (15.54)]. We now insert this decomposition into Eq. (15.120):

$$R = R_0 + R_0 U (P + Q) R = R_0 + R_0 U PR + R_0 U QR. \qquad (15.121)$$

In order to eliminate the irrelevant part of the resolvent, we project both sides of (15.121) on the irrelevant state:

$$QR = QR_0 + QR_0 U PR + QR_0 U QR \qquad (15.122)$$

This is regarded as an equation for the irrelevant part, of the form $QR = a + bQR$; it can be solved by successive iterations:

$$QR = \sum_{m=0}^{\infty} (QR_0 U)^m \{QR_0 + QR_0 U PR\}. \qquad (15.123)$$

This expression is substituted into (15.121) and rearranged as follows:

$$R = R_0 + R_0 U \sum_{m=0}^{\infty} (QR_0 U)^m QR_0 + R_0 U \sum_{m=0}^{\infty} (QR_0 U)^m PR. \qquad (15.124)$$

We now introduce the *"irreducible evolution operator"* $\mathcal{E}(z)$:

$$\mathcal{E}(z) = \sum_{m=0}^{\infty} U [QR_0(z)U]^m \qquad (15.125)$$

This operator has a structure that resembles the resolvent; its expansion (15.125) describes multiple transitions produced by the operator U. Its characteristic feature is the occurrence of the operator Q: it *prevents the passage through the privileged state in all intermediate states.*

Using (15.125) in (15.124), we find the following equation for the resolvent:

$$R = R_0 + R_0 \mathcal{E} Q R_0 + R_0 \mathcal{E} PR. \qquad (15.126)$$

We note the important fact that *only the relevant part PR of the resolvent appears in the right hand side of Eq. (15.126).* This has two direct consequences.

A). *The irrelevant part QR is entirely expressed in terms of the relevant one,* by the following expression obtained by projecting (15.126) on the irrelevant space:

$$QR = QR_0 + QR_0 \, \mathcal{E} \, QR_0 + QR_0 \, \mathcal{E} \, PR. \qquad (15.127)$$

B). *The relevant part PR obeys a closed equation:*

$$PR = Pz^{-1} + Pz^{-1}\mathcal{E}\,Qz^{-1} + Pz^{-1}\mathcal{E}\,PR, \qquad (15.128)$$

where the explicit form of $R_0 = z^{-1}$ is inserted. The solution of this equation is:

$$PR(z) = P\,\frac{1}{z - P\mathcal{E}(z)P}\left[P + Pz^{-1}\mathcal{E}(z)\,Q\right]. \qquad (15.129)$$

Combining this with Eq. (15.127) we find:

$$QR(z) = Qz^{-1}\left[1 + \mathcal{E}(z)\right]Q + Qz^{-1}\mathcal{E}(z)\,P\,\frac{1}{z - P\mathcal{E}(z)P}\left[P + Pz^{-1}\mathcal{E}(z)\,Q\right] \qquad (15.130)$$

It is now easy to prove the equivalence of this equation with (15.56). We introduce the *propagation fragment* [see (15.57)]:

$$\begin{aligned}
Q\mathcal{P}(z)Q &= \sum_{m=0}^{\infty} Q\,z^{-m-1}\left[QUQ\right]^m Q \\
&= Qz^{-1}\mathcal{E}(z)Q = Q\frac{1}{z - QUQ}Q \qquad (15.131)
\end{aligned}$$

Next we note:

$$\begin{aligned}
P\mathcal{E}(z)P &= \sum_{m=0}^{\infty} PU\left[Q\,z^{-1}U\right]^m P \\
&= PUP + PUQ\sum_{m=0}^{\infty} z^{-m-1}\left[QUQ\right]^m QUP \\
&= PUP + PUQ\frac{1}{z - QUQ}QUP \\
&= PUP + PUQ\mathcal{P}(z)QUP, \qquad (15.132)
\end{aligned}$$

n agreement with (15.58). The same type of calculations yield the definitions of the :reation fragment and of the *destruction fragment* as given in (15.59) and (15.60):

$$\begin{aligned}
Q\mathcal{C}(z)P &= z^{-1}Q\mathcal{E}(z)P = Q\mathcal{P}(z)QUP, \\
P\mathcal{D}(z)Q &= z^{-1}P\mathcal{E}(z)Q = PUQ\mathcal{P}(z)Q.
\end{aligned}$$

Introducing all these partial results into (15.129) and (15.130), the combination of hese equations yields precisely Eq. (15.56) of the main text.

15.6 Bibliographical Notes BN15

Among the numerous publications devoted to the maps, and more specially to the *standard map*, we single out the following ones:

Chirikov, B., 1979, Phys. Reports, **52**, 265,

Lichtenberg, A.J. and Lieberman, M.A., 1983, *Regular and Stochastic Motion*, Springer, Berlin,

MacKay, R.S., Meiss, J.D. and Percival, I.C., 1984, Physica D **13**, 55,

Ott, E., 1993, *Chaos in Dynamical Systems*, Cambridge Univ. Press,

MacKay, R.S., 1993, *Renormalisation in Area-preserving Maps*, World Scientific, Singapore.

The important work of Greene is:

Greene, J.M., 1979, J. Math. Phys., **20**, 1183.

General discussions of the *Perron-Frobenius operator* are found in:

Lasota, A. and Mackey, M.C., 1985, (BN7),

Hasegawa, H.H. and Saphir, W.C., 1992, Phys. Rev. A **46**, 7401,

Nicolis, G., 1995, *Introduction to Nonlinear Science*, Cambridge Univ. Press.

The special representation of the *resolvent operator* appearing in this chapter is based on the analogous treatment of the Liouville resolvent in statistical mechanics:

Prigogine, I., George, C. and Henin, F., 1969, Physica, 45, 418,

Balescu, R., (RB-2): BN1.

The initial works on the *standard map diffusion coefficient* are:

Rechester, A.B. and White, R.B., 1980, Phys. Rev. Lett., **44**, 1586,

Rechester, A.B., Rosenbluth, M.N. and White, R.B., 1981, Phys. Rev. A **23**, 2994,

Meiss, J.D., Cary, J.R., Grebogi, C., Crawford, J.D., Kaufman, A.N. and Abarbanel, H.D.I., 1983, Physica, **6 D**, 375; see also: Lichtenberg and Lieberman (quoted above).

The basic derivation given here follows:

Hasegawa, H.H. and Saphir, W.C., 1991, in: *Aspects of Nonlinear Dynamics* (I. Antoniou and F. Lambert, eds.), Springer, Berlin.

The *subdiffusive regime* and the corresponding *CTRW model* were studied in:

Balescu, R., 1997, Phys. Rev. E (to be published, 1997).

The *superdiffusive regime* was studied in:

Ichikawa, Y.H., Kamimura, T. and Hatori, T., 1987, Physica **29 D**, 247,

Horita, T., Hata, H., Ishizaki, R. and Mori, H., 1990, Progr. Theor. Phys., **83**, 1065,

Ishizaki, R., Horita, T., Kobayashi, T. and Mori, H., 1991, Progr. Theor. Phys., 85, 1013,

Zumofen, G. and Klafter, J., 1994, Europhys. Lett., 25, 565.

Chapter 16

Conclusions

16.1 The Status of Statistical Dynamics

It used to be claimed twenty years ago that "equilibrium STATISTICAL Mechanics" is mainly statistical, whereas "nonequilibrium Statistical MECHANICS" is mainly mechanical. This implies that in equilibrium theory, the role of dynamics is trivial: it just tells us that the ensemble distribution function is a function of the Hamiltonian. The choice of the specific function (canonical, grand canonical,...) and the link with thermodynamics (Boltzmann's entropy formula, the relation between partition function and free energy,...) are provided by statistical arguments. In nonequilibrium theory the roles are, in principle, reversed. The goal of the theory is to understand the evolution laws of macroscopic systems in terms of the dynamics of a large set of molecules: ideally this should be realized without any *ad hoc* modification of the microscopic dynamical laws. Needless to say, the solution of the general problem formulated in this way is a hopeless enterprise.

The way out of the dilemma is *to ask Nature the proper questions, i.e., those for which an answer is meaningful and verifiable at the macroscopic level.* This point of view implies deliberately renouncing to look for a complete solution of the dynamical problem. Statistical dynamics thus necessarily implies a series of *successive contractions of the description of a many-body system.* We are pruning off the dangling branches of the theory, trying to keep only those that may be expected to bear fruit. Let me stress that this is NOT an admission of helplessness. Even if we were able (through a miracle) to trace in time the position of each of the 10^{23} particles of the system under consideration, this would NOT help us in understanding why a fluid behaves diffusively, let alone in calculating the diffusion coefficient. On the other hand, if we had a theory that would tell us that, after some time (which can be quantified), the violently complicated motion "calms down" and that on the "long time scale" there remains a diffusive type of motion, I personally am quite satisfied.

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The reader may wonder why suddenly I am turning to a personal style ("I" instead of "we"). The fact is that in this matter there is not yet a universal agreement among workers in the field. The reason is the difficult problem of the *"paradox" of irreversibility*, i.e., understanding the emergence of irreversible macroscopic evolution laws from the reversible Hamiltonian dynamics of the particles.

The evolution of a distribution function is determined by the Liouvillian which (multiplied by i) is a Hermitian operator. Most physicists, used to traditional quantum mechanics, said that the Liouvillian can only have real eigenvalues, hence it cannot express dissipation, which requires complex eigenvalues with a negative imaginary part. In this statement, one had simply forgotten that the nature of the eigenvalues of an operator also depends on the functional space to which the target functions belong. One used to be so much attached to Hilbert spaces, that most often one assumed without saying that the distribution functions of statistical mechanics belonged to a Hilbert space. It should have been clear, on the other hand, that such a requirement would be, to say the least, unnnatural, and certainly not imposed by the postulates of statistical mechanics. The state of a system is defined by a phase space function $F(q, p; t)$ of which only normalization (3.7) is required; nothing is said about the integral of its *square* (or any other properly defined scalar product with itself). The complementary element of the theory is the set of dynamical functions $b(q, p)$; for these no integral properties are specified. The only objects to which a (macroscopic) meaning is given are the averages (3.14), which are *"mixed"* objects: integrals of a product of $b(q, p)$ and $F(q, p; t)$, i.e. things that are "living" in different functional spaces. We are far from a Hilbert space structure! The structure rather resembles a kind of Banach space with dynamical functions playing the role of "bra's" and distribution functions the role of "kets". A minimal remark is then the following: it is known that there exist functional spaces in which Hermitian operators have complex eigenvalues. This then suffices to lift the main objection to irreversibility, without any need to think of new laws of physics. It is on this important property that Prigogine and his coworkers build their recent theory of irreversibility (see below).

As stated in the introduction, I do not wish to enter here the debate on the origin of irreversibility, or the nature of time. This kind of discussion very easily drifts away from physics. As I am not very philosophically minded, I prefer to avoid any such extrapolations.

Remaining on firm ground, I chose to present in the second part (Chaps. 6 to 9), in the announced pragmatic spirit of this book, the very simplest form of derivation of irreversible kinetic equations. Of course, this implies a limitation to a certain class of systems and of state parameters (density, temperature,...) such that the first two conditions of Sec. 6.4 are satisfied, namely:

a) There exists a small parameter in the problem [1];

b) The interactions and the correlations have a finite range.

These conditions ensure the existence of two widely separated time scales [2] (duration of a collision, and relaxation time). Whenever the conditions are satisfied, a rigorous asymptotic analysis of the truncated hierarchy leads to a kinetic equation as defined in Chap. 9, describing an irreversible evolution[3], combined with motion described by the free flow term and the Vlasov term. It is sometimes said that in this type of derivation *irreversibility appears as the result of an approximation.* I believe that this is a misinterpretation. First, nobody has ever been able to make a mathematically rigorous statement, without any approximation, about the behaviour of a set of 10^{23} particles. Next, once a system has been chosen and all simplifications resulting from the smallness of the parameter have been done in the beginning, the mathematical treatment of the resulting simplified system is quite well defined. It represents a way of singling out the most "robust" mode of evolution, that survives after a sufficiently long time, when the complicated short time-scale motions have been damped or phase-mixed by destructive interference. The result of this treatment is the derivation of explicit equations of evolution (Chaps. 6 - 8) having the properties one would have liked to find (Chap. 9) and which are a well-defined starting point for the calculation of transport coefficients (Chap. 10), hence for a comparison with experiment. It may also be mentioned that these systems, in which there exists a small parameter, are the only ones for which a fully rigorous mathematical treatment can be given (see BN16).

One would then naturally ask: what can be done in more general cases, when at least one of the assumptions is violated? Clearly, in this case the asymptotic method may become dubious, because the various time scales come closer together. Possible generalizations can be (and have been) done along various lines.

16.2   Toward a Grand Theory of Irreversibility ?

A) Series Expansions

The first track any physicist would follow is to devise some form of perturbation expansion, by which he would obtain systematic corrections in successive orders of the moderately small parameter. This method was briefly discussed in connection

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simply a plain parameter like the charge or the density that is supposed small, but possibly some subtle combination of these.

[2] For inhomogeneous systems we need an additional assumption on the smallness of the gradients to ensure the existence of a third, much longer hydrodynamic time scale, allowing the definition of a hydrodynamic regime.

[3] A similar asymptotic analysis allowed us to single out the diffusive mode in the standard map in Sec. 15.2.

with the kinetic equation of moderately dense gases (BN7). This method has some severe drawbacks, which makes it a bad candidate for a "Grand" kinetic theory.

From the practical point of view, the calculational difficulties become very rapidly prohibitive. As can be easily guessed from the reasonings in Chaps. 6 and 7, every additional order in the coupling parameter or in the density will introduce a correspondingly higher order of the correlations; hence, an increasing number of equations must be retained in the BBGKY hierarchy. Most workers will rightly consider that the enormous amount of work put into this problem (having to deal with three-body or four-body collisions) is not worth a final tiny correction that would be barely observable experimentally.

A more fundamental difficulty comes from the fact that this method necessarily assumes that the various physical quantities that can be calculated are *analytic functions* of the small parameter. Clearly, there is no *a priori* reason why Nature should be so kind to us! And, sure enough, She isn't! This discovery came as a shock in the sixties when it was found that the transport coefficients of a dense gas, when expressed as power series in the density (virial expansion), lead to divergences (see the brief discussion in BN7).

B) Projection Techniques

In my 1975 book (RB-2) I developed in great detail a presentation of the kinetic equations based on a subtle decomposition of the distribution functions. This theory was inspired from ideas of Prigogine and George, but it pursued a less ambitious goal than their work and it uses a quite different representation of the state of the system (reduced distribution function instead of Fourier components of the phase space distribution). I still believe this is a satisfactory theory, giving a clear picture of the structure of kinetic theory, in spite of its limitations. I shall not repeat here this matter, because the purpose of the present book is different; I thus give just a brief summary and refer the reader to RB-2 for the details.

The complete set of reduced distribution functions (RDF) can be grouped together in a *distribution vector* **f**, which can be projected on various subspaces. (The idea of this projection technique is the same as in Sec. 15.3.) A first decomposition consists of separating the *vacuum component* $V\mathbf{f}$ and the *correlation component* $C\mathbf{f}$. The former is the term factorized into a product of one-particle RDF's. Thus, in Eqs. (4.37), (4.38) the vacuum part is the collection of the first terms in the right hand sides, all the remaining terms forming the correlation component. The decomposition can be thought of as being realized by the action of two operators acting as *projection operators*, with the following properties:

$$V^2 = V, \quad C^2 = C, \quad VC = CV = 0, \quad V + C = I. \qquad (16.1)$$

It is important to note that the unperturbed Liouvillian conserves the type of correlations: if $L'_{jn} = 0$ in Eqs. (4.41), (4.44), these equations are closed and diagonal in f_1, g_2, etc. This is expressed by saying that the unperturbed Liouvillian operator $\mathcal{L}^0$ commutes with the vacuum projector V (hence also with C):

$$V\mathcal{L}^0 = \mathcal{L}^0 V. \tag{16.2}$$

Whenever interactions are present the vacuum is coupled to the correlations, as is clearly seen in Eqs. (4.41), (4.42). One can say pictorially that the interactions create, propagate, transform or destroy correlations. The vacuum part of the distribution vector thus obeys an equation of evolution, written compactly as follows, by using (16.1), (16.3):

$$\partial_t V\mathbf{f} = \mathcal{L}^0 V\mathbf{f} + V\mathcal{L}'V\mathbf{f} + V\mathcal{L}'C\mathbf{f}. \tag{16.3}$$

[Eq. (4.41) is the one-particle component of this vectorial equation; one clearly recognizes the three terms corresponding precisely to (16.3)]. This equation clearly exhibits the main difficulty of the problem: *there is no exact closed equation for the vacuum component of the distribution vector, thus no kinetic equation for the one-particle RDF.*

The way out of this dilemma is to look for an alternative decomposition, effected by two other projectors Π, $\tilde{\Pi}$, which are invariant under the *complete* Liouvillian $\mathcal{L} = \mathcal{L}^0 + \mathcal{L}'$. Thus Eqs. (16.1), (16.2) are generalized as follows:

$$\Pi^2 = \Pi, \quad \tilde{\Pi}^2 = \tilde{\Pi}, \quad \Pi\tilde{\Pi} = \tilde{\Pi}\Pi = 0, \quad \Pi + \tilde{\Pi} = I, \tag{16.4}$$

and:

$$\Pi\mathcal{L} = \mathcal{L}\,\Pi. \tag{16.5}$$

The projector Π clearly depends on the interaction potential, hence on the coupling parameter λ. The following "boundary condition" is required in order to construct a unique operator:

$$\lim_{\lambda \to 0} \Pi = V. \tag{16.6}$$

It appears that a projection operator having all these properties exists, can be constructed explicitly as an infinite perturbation series in powers of λ, and is indeed unique. It produces a decomposition of the distribution vector as: $\mathbf{f} = \Pi\mathbf{f} + \tilde{\Pi}\mathbf{f}$; the part $\Pi\mathbf{f}$ is called the *kinetic component* of the distribution vector.

The kinetic component can, in turn be decomposed into a vacuum part and a correlation part:

$$\Pi f = V\,\Pi f + C\,\Pi f. \tag{16.7}$$

Now comes "the miracle": *the vacuum part of the kinetic component* $V\,\Pi f$ *obeys a closed, markovian equation of evolution!*

$$\partial_t V\,\Pi f = V T V\,\Pi f. \tag{16.8}$$

This is precisely the kinetic equation we were looking after. The explanation is the following: the evolution of $V\,\Pi f$ is actually coupled to $C\,\Pi f$ as in (16.3), but the correlation part of the kinetic distribution vector is a functional of the vacuum. This property was first stated by Bogoliuobov as an assumption, defining the "kinetic regime": it appears here as an exact property of the kinetic component of f. We thus recognize the features encountered in our earlier derivations. When the operator VTV is made explicit for the various known limiting cases (weak coupling, small density, small plasma parameter), the corresponding kinetic equations are recovered. As for the complementary part, $\bar{\Pi} f$, it is shown that it is vanishing in equilibrium, and that it does not contribute to the transport coefficients.

We do not pursue this discussion here: the details and the proofs are found in RB-2. Let us, however, stress that this structure is *not universal* [4]: it requires that certain, rather abstract conditions be satisfied by the resolvent (hence by the interaction potential), ensuring the mathematical existence of the collision operator. It is impossible to give general, explicit criteria for their fulfilment; in RB-2 a non trivial case has been checked completely, showing that the theory is not void.

C) Spectral Representation of the Liouville Operator

Prigogine and his coworkers went further, trying to realize a much more ambitious project. First, in collaboration with C. George, F. Henin and L. Rosenfeld, the decomposition into Π and $\bar{\Pi}$ was further refined by introducing an infinite number of projectors: instead of grouping together all the correlation functions, a projector $\Pi^{(n)}$ was attached to each correlation function. It was then shown that each "kinetic correlation" obeys a separate evolution equation (a *"subdynamics"*) decorrelated from all the others. By means of a *non-unitary transformation*, the evolution operators are brought in the form of irreversible collision operators (this step was put into nice mathematical form by B. Misra, I. Prigogine and M. Courbage). The last, most daring step was taken by I. Prigogine with (among others) T. Petrosky, I. Antoniou, S. Tasaki and H. Hasegawa . Their purpose was the complete solution of the eigenvalue problem of the Liouville operator and the construction of a spectral representation of this operator. The first, crucial point was to realize that for the

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[4]It should not be! The solar planetary system is certainly not behaving like a gas in the kinetic regime!

basic understanding of irreversibility it was necessary to extend the functional space of statistical mechanics beyond the "sacred" Hilbert space. Following the mathematical work of I. Gelfand and N. Vilenkin and the physical work (in quantum mechanics, and also with suggestions to statistical mechanics) of A. Böhm, the authors quoted above consider that the "natural" space of statistical mechanics is a *rigged Hilbert space*, in which singular functions (such as delta distributions) can be properly defined.[5] In such a space (as mentioned above) the Hermitian Liouville operator may have complex eigenvalues. The authors then show that the subdynamics decomposition leads to the spectral decomposition they are looking for, with a definition of the complex eigenvalues and a set of right and left eigenvectors. The method was applied to two types of systems: very simple chaotic maps (such as: Bernoulli, tent, baker, standard,...) and "large Poincaré systems" (see below), classical and quantum.

I cannot present these recent, very technical results in the present elementary book. I therefore limit myself to a few remarks, and refer the reader to the works quoted in BN16. I feel quite satisfied with the applications to the study of chaotic maps. Here a very complete, explicit and elegant solution has been given; the decaying eigenvalues appear to be related to the Lyapounov exponents of the maps, hence to their intrinsic instability. The authors thus achieved a significant progress and clarification of the relation between dynamical instability and irreversibility in these systems. Unfortunately, a Bernoulli map or a baker map are far from a real physical system of particles (only the standard map has some connection with a model of some physical phenomena, see Chap. 15).

The situation with *"large Poincaré systems"* (LPS) is different. These are defined as large systems of particles exhibiting resonances, i.e. small denominators in the perturbation expansion of their propagator. The LPS is thus a valid model for a large class of material systems: all systems considered in the second part of our book are LPS. The work of Petrosky and Prigogine is, however, not complete and certainly not as rigorous as their treatment of simple maps. It is restricted to spatially homogeneous systems; the extension of their method (based on Fourier transforms) to inhomogeneous systems is certainly not trivial. Their treatment of the thermodynamic limit (an essential ingredient for "large" systems) is open to objections, which I shall not discuss here.

Finally, I wish to make some remarks which should help, I hope, avoiding some serious misunderstandings. In the works quoted here one very often sees statements claiming "new (non-Newtonian) laws of classical mechanics, incorporating irreversibility at the very start, in which there are no trajectories"; moreover, the new laws "ex-

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[5]This is the "next simplest choice" after the Hilbert space. It is, however, not necessarily the most natural space for statistical mechanics. In particular, it does not obviously stress the difference between distribution functions and dynamical functions, according to our remark at the beginning of this section.

ress possibilities and no more certitudes". First, even the wild behaviour of chaotic systems is a consequence of classical mechanics, as shown by Ia. Sinai in the case of the billiards: there is no need of a new basic law, only a precise elaboration of the consequences of Newtonian mechanics is required. The statement about trajectories is particularly misleading to me. As long as we admit the existence of atoms (modelled as point particles) it is impossible to deny the fact that, at each time, each particle is "somewhere", at a well-defined position. It is true that, in some circumstances, we may not be able to *predict* the trajectory, because we are not able to repeat an experiment in which *all* the particles have *exactly* the same initial condition. In a chaotic system, the slightest error will be exponentially amplified. But clearly, *unpredictability does not imply inexistence*. We are here in a situation like Brownian motion described by Langevin equations (Chap. 11). A well-defined orbit can be determined by solving the equation for a given realization of the random force; but the orbit will be different in each realization. What the authors really mean is that, having constructed a statistical theory of these (unstable) dynamical systems, it is not possible to use a distribution function of the form $F(q, p; t) = \Pi \delta[q - q(t)] \delta[p - p(t)]$ without leaving the functional space chosen for the representation of the system.

Finally, I feel uneasy with overemphasizing the chaotic nature of material systems to begin with, there is no proof that a collection of N interacting particles is a chaotic system (in the technical sense). In particular, I see the following difficulty. Real molecules or atoms are not point particles, but rather a collection of nucleons and electrons having a non-zero extension in space. If their collection is chaotic, i.e., exhibits sensitive dependence on initial conditions, how do the molecules conserve their identity, rather than exploding along exponentially diverging orbits?

)) Maximum entropy theory

I now very briefly mention an alternative attempt towards a 'grand theory' developed by E.T. Jaynes and his coworkers. This approach was originally inspired by Gibbs' philosophy of equilibrium statistical mechanics (Chap. 1). In a first step it involves the determination of the "most plausible" initial condition at $t = 0$, given a limited amount of information. This is done by maximizing the entropy, taking into account the information about the state of the system at some previous times. If this initial condition is let to evolve according to the Liouville equation (hence at constant entropy), it will not explain irreversibility. One therefore repeats this process of entropy maximization at successive later times $t_1 < t_2 < ...$: an increase of entropy results. But this process, which amounts to changing the law of evolution at the most elementary level, is not acceptable. Besides being quite arbitrary, this evolution law is not transitive: the one-step evolution from 0 to t_2 does not yield the same result as the evolution from 0 to $t_1 < t_2$, followed by an evolution from t_1 to t_2. Although some of the difficulties can be cured, the resulting theory lacks a solid foundation; it

is, moreover, extremely complex and has not led to any new concrete results.

One sees how easily the debate on these themes may drift toward philosophical difficulties whenever the physics becomes very involved and does not (yet!) provide us with unambiguous answers. I therefore stop here this discussion.

16.3 "Stochastic Statistical" Dynamics

This title contains a crude, but deliberate pleonasm. It represents rather well the philosophy of the second part of the book, starting at Chap. 11. The attempts toward a "grand theory" are very interesting from the point of view of principles, but necessarily remain quite formal and academic. We should recognize that the existing "grand theories" provide no *general and rigorous derivation* of statistical mechanics from molecular dynamics, valid for *arbitrary systems*. No explicit kinetic equation arose from this line of work. On the other hand, physicists are eager to study new problems going beyond the "classics"; these problems necessarily become more and more complex.

If we are to attack such problems, we are bound to be less ambitious! If we look for an analytical theory of turbulent transport from first principles, we would probably have to wait for a couple of centuries (thus die before getting the beloved answer!)

Probabilistic arguments are not to be excluded from statistical dynamics, but they should not be declared as "fundamental": they can only be considered, more modestly, as helping to *model* the behaviour of complex dynamical systems. Knowing that stochastic laws can be derived for simple systems, a probabilistic law of evolution can be conjectured, without proof. It then acquires the logical status of a *postulate*, whose consequences must be tested directly against experiment.

Once a reasonable set of working assumptions are accepted, the way is open for non-trivial physics. These assumptions have to do with the "degree of randomness" admitted *a priori* for the description of the system's law of evolution. (It is precisely this enhanced role of probabilistic features that I wanted to stress by the strong pleonasm in the title of this section). Thus, one could adopt a "semi-dynamical" point of view like in the Langevin equation (Chap. 11): a Newton equation with a random force. Or else, one could describe the dynamics by purely probabilistic rules, like in the continuous time random walks (Chap. 12). A more extreme, but philosophically quite different simplification is the replacement of the dynamical equations by a low-dimensional map exhibiting deterministic chaos (Chap. 15). In all these cases the working assumptions are sufficiently clear and their adoption (or experimental verification) poses no serious problems of conscience.

These problems and methods have yielded an exciting set of results in recent years. Most fascinating are the non-classical features discovered here: non-Gaussianity of the basic stochastic processes, role of non-Markovian equations of evolution, role of

fractal structures, emergence of "strange transport", etc. We are only beginning to uncover an extremely rich domain of problems. Coming back to the first sentence of this chapter, we can see that nonequilibrium statistical mechanics has nothing to lose, and very much to gain by becoming "more statistical". It is the inclusion of this wider methodology that I wanted to stress in using the new name of STATISTICAL DYNAMICS.

16.4   Bibliographical Notes BN16

As stated in the main text, my position in the debate on irreversibility remains very close to the ideas expressed in my previous book RB-2 (BN1), modulated by the results of recent works.

The basic assumption that the correlation part of the state vector is a functional of the vacuum part in the kinetic regime was introduced by Bogolioubov, N.N., 1946 (BN5).

A recent book presenting all the presently known "rigorous results" for the construction of a statistical dynamics by means of true mathematical theorems is:

Spohn, H., 1991 (BN3).

The following references to the works of I. Prigogine and his collaborators only include the main milestones; additional references will be found in these works.

The idea of subdynamics (with an infinite number of components) was introduced and developed in:

George, C., 1967, Bull. Cl. Sciences, Acad. Roy. Belg., 53, 623,
Prigogine, I., George, C., Henin, F. and Rosenfeld, L., 1973, Chemica Scripta, 4, 5.

The resulting relation between dynamics and stochastic evolution via a non-unitary transformation was elegantly formulated in:

Misra, B., Prigogine, I. and Courbage, M., 1979, Physica, 98 A, 1.

The concept of a rigged Hilbert space is presented in:

Gelfand, I. and Vilenkin, N., 1964, Generalized Functions, vol. 4, Academic Pr., New York,
Böhm, A., 1978, The Rigged Hilbert Space and Quantum Mechanics, Springer Lecture Notes in Physics, vol. 78, Springer, Berlin.

The application of rigged Hilbert spaces to chaotic maps is given in:

Antoniou, I. and Tasaki, S., 1993, Internat. J. of Quant. Chemistry, 46, 425,
Hasegawa, H.H. and Saphir, W.C., 1991, 1992 (BN15),

Gaspard, P., 1992, J. Phys. **A 25**, L483,

Hasegawa, H.H. and Driebe, D.J., 1994, Phys. Rev., **E 50**, 1781.

"Large Poincaré systems" are treated in:

Petrosky, T. and Prigogine, I., 1993, Proceed. Natl. Acad. Sci. USA, **90**, 9393,

Petrosky, T. and Prigogine, I., 1995, Chaos, Solitons and Fractals.

"Semi-popular" expositions of these recent developments are given in:

Prigogine, I., 1994, *Les lois du chaos*, Flammarion, Paris,

Prigogine, I., 1996, *La fin des certitudes*, O. Jacob, Paris.

The *maximum entropy* approach to statistical mechanics is found in:

Jaynes, E.T., 1983, *Papers on probability, statistics and statistical mechanics*, (D. Rosenkrantz, ed.), D. Reidel, Amsterdam,

Grandy, W.T., 1980, *Principle of maximum entropy and irreversible processes*, 2 vols., D. Reidel, Amsterdam.

A somewhat related approach is developed by:

Zubarev, D.N., 1974, *Non-equilibrium statistical thermodynamics*, Plenum, New York.

A very interesting comparison of the various "grand theories" is given by:

Dougherty, J.P., 1994, Phil. Trans. Roy. Soc. London, **346**, 259.